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INGEGNERIA CHIMICA E DEI PROCESSI INDUSTRIALI**

**PYROLYSIS OF PEAT:
AN EXPERIMENTAL INVESTIGATION**

Relatore: Prof. Fabrizio Bezzo
Correlatore: Prof. Frej Bjondahl

Laureanda: MARTA CUNICO

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Abstract

The objective of this Thesis is to explore the operating conditions (in particular, temperature and residence time in the reactor) in the pyrolysis of peat so as to obtain solid products (char) suitable for industrial utilisation. Results show that the yield of char diminishes when the temperature increases or when a higher reactor residence time is adopted.

However, the study also highlighted that an increase in the operative temperature can determine an unacceptable energy expenditure. The exploitation of secondary products (tar and gases) may (partly) compensate for this.

The study was done in the Process Design and Systems Engineering Department in Åbo Akademi University (Turku, Finland), with the help of the professors Jarl Ahlbeck and Frej Bjondahl.

Riassunto

La torba è un materiale organico formatosi dalla decomposizione di materiale vegetale impregnato d'acqua in condizioni anaerobiche. Le sue caratteristiche dipendono fortemente dal luogo di origine del materiale e dal suo grado di decomposizione: in particolare, più quest'ultimo valore è alto, più la torba sarà simile al carbon fossile. È per questo motivo che negli ultimi anni la ricerca di possibili applicazioni di questo materiale nell'industria chimica sta aumentando, soprattutto negli stati carenti di fonti di combustibili fossili (come la Finlandia).

Lo studio riportato in questa Tesi è stato effettuato nel Dipartimento "Process Design and Systems Engineering" in Åbo Akademi University (Turku, Finlandia), durante un periodo di studio all'estero con il programma Erasmus.

Il documento è composto da tre sezioni: nella prima viene descritta la torba e le sue caratteristiche come biomassa (ponendo l'attenzione su come essa possa essere utilizzata nei processi chimici), mentre la seconda tratta in maniera più approfondita il processo di pirolisi. La terza sezione, invece, racchiude parte sperimentale del lavoro: dapprima sono stati analizzati quattro campioni di torba prelevata da Karvia (in Finlandia), misurando il loro grado di umidità, il potere calorifico, il contenuto di ceneri e le percentuali di carbonio, idrogeno, zolfo, azoto e ossigeno presenti, in modo da poter determinare il grado di decomposizione di essa e di poter scegliere la materia prima più adatta per i successivi esperimenti. Successivamente si è proceduto con gli esperimenti di pirolisi: dopo aver selezionato due campioni di torba, sono state effettuate 8 prove per campione a diverse temperature finali (150°C, 267°C, 383°C, 500°C) e a diversi tempi di residenza nel reattore (0 minuti, dove il campione viene tolto immediatamente al raggiungimento della temperatura massima, e 10 minuti).

Lo scopo del lavoro è di analizzare come variano la resa organica, la resa energetica e la resa di carbonio del carbone prodotto dalla pirolisi al variare di alcuni parametri (temperatura e tempo di residenza). In particolare si è osservato che:

- la resa organica (ossia la quantità di carbone prodotto per quantità di torba utilizzata nell'esperimento) diminuisce all'aumentare della temperatura (da 99.60% a 86.17%);
- la resa energetica (ossia il potere calorifico totale dei prodotti solidi per il potere calorifico iniziale della torba) diminuisce all'aumentare della temperatura (da 97.20% a 96.50%);
- la resa di carbonio (quantità di carbonio presente nei prodotti solidi per quantità di carbonio presente nella torba iniziale) diminuisce all'aumentare della temperatura (da 94.75% a 90.93%).

All'aumentare del tempo di residenza, queste differenze diventano più marcate.

È stato inoltre proposto un bilancio di materia in base al modello "one step global model" (dove la costante cinetica è di tipo Arrhenius) ed è stata stimata l'energia necessaria per la pirolisi a diverse temperature e tempi di residenza. Il tempo di permanenza della torba nel reattore, infatti, ha una forte influenza sul fabbisogno energetico del processo: è stato calcolato, infatti, che a 500°C la pirolisi richiede poco più di 1.5 MJ se il campione viene tolto immediatamente dal reattore al raggiungimento della temperatura, mentre raggiunge i 14 MJ se lo si lascia per 10 minuti. Questi risultati vanno tenuti in considerazione nella scelta della destinazione finale dei prodotti: un carbone con alte percentuali di carbonio prodotto a temperature elevate richiede una notevole quantità di energia e sarà perciò utilizzato in processi che richiedono un certo grado di qualità della materia prima (come nella produzione di catalizzatori o nei processi elettrochimici), mentre per processi di combustione può essere utilizzato un carbone prodotto a basse temperature, in quanto più economico.

Occorre tener presente che, affinché la pirolisi diventi un processo economicamente interessante, conviene integrarla con altri processi che prevedano il recupero degli altri prodotti liquidi e dei gas, in modo da coprire i costi energetici. In questo modo il carbone formato dalla torba diventa un'interessante fonte di solo carbonio per le industrie che vogliono cercare un'alternativa più sostenibile al comune carbon fossile.

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Introduction

In the last years a lot of research has been made to improve the utilization of biomasses, mostly in countries that lack domestic sources of either coal or petroleum. Finland is one of them: it is a country where the supply of fossil fuels is given mostly by importation, but it is an incredible source of peat (as its name literally says in Finnish: “peatland”), that can be utilised in several chemical processes.

In this Thesis, in particular, the pyrolysis of peat is studied, with a specific attention to the char production. Nowadays, this solid product is mainly used as a fuel for combustion: the interest is to see if it is possible to destine it to different uses, as gasification. To do that, the characteristics of the final char obtained at different temperatures and residence times in the reactor are examined.

In Chapter 1 the characteristics of peat as a raw material are described; while in Chapter 2 there is an overview of the most important chemical processes that use biomasses as feedstock: combustion, gasification and pyrolysis. This last one is presented in details in Chapter 3.

The experimental part of the work is contained in Chapter 4: in the beginning there is an analysis of the four samples of peat used in this study; then the data of the pyrolysis process at different temperatures and residence time are reported. In addition, there is a simplified mass and energy balance. In the Conclusions, the main results are commented on.

The work made in this Thesis was done in the Process Design and Systems Engineering Department in Åbo Akademi University (Turku, Finland).

Chapter 1

Peat Characteristics

Finland is the country with the highest proportion of wetlands in the world (Figure 1.1), and they have been used for a long time for commercial extraction for horticulture, soil improvement and fuel production (the peatland has a total area of 89 000 km², of which 6 220 km² is potentially suitable for commercial extraction, and 78% of that is suitable for fuel peat production¹).

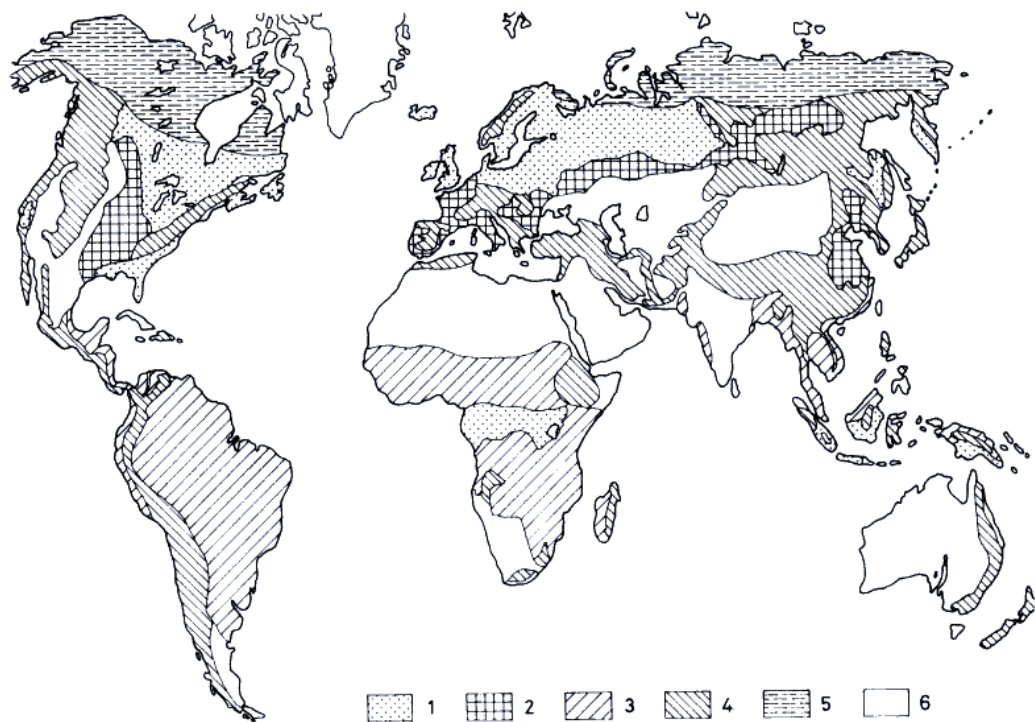


Figure 1.1. Major peat areas. 1=Regions with intensive peat accumulation; 2=Regions with minor peat accumulation; 3=Tropical and subtropical areas with little peat accumulation; 4=Mountain areas with little peat accumulation; 5=Polar areas with a low rate of peat accumulation; 6=Regions without peat accumulation.

(<http://www.scopenvironment.org/downloadpubs/scope13/chapter06.htm>
¹, last visit: 14/11/2014)

Peat is usually used as a fuel (it is directly burned), or as a natural fertilizer for plants and flowers. Nowadays the interest is to create a process to transform peat

¹ <http://www.peatsociety.org/peatlands-and-peat/global-peat-resources-country>

into a gaseous or liquid fuel, to reduce the carbon dioxide emissions from fossil coal and natural gas, but also to find an alternative “sustainable” resource.

Peat is an organic deposit formed from more or less decomposed plant material in anaerobic water-saturated conditions. The degree of decomposition (humification) influences strongly its appearance, but also its characteristics. A poorly decomposed peat contains a considerable amount of fibrous material and exhibits a cellular structure under the microscope, while highly humified peat appears as a dark amorphous dispersed mass: its look (and its characteristics) will be more similar to the feature of coal. In effect, peat is classified geologically as an intermediate stage between plant substance and coal (Roy et al., 1983). The degree of humification and the composition is dependent on the location and the geological history: in a warm climate, for instance, the plant material decomposes quickly, so it will be more probable to find highly decomposed peat.

1.1 Physical and chemical properties of peat

As said before, peat can be more similar to wood or coal depending on the degree of decomposition of it (if the humification degree is very high, peat will be more chemically similar to lignite). This depends on different factors, such as the original plant (from where the peat comes), but above at all the depositional environment. Indeed, peat formed in a cold and humid environment decomposes slowly (so it will have a low degree of decomposition), while in a dry and hot climate it is more likely to be highly decomposed. It is important to notice that the “degree of decomposition” (or humification) is a data correlated to the amount of amorphous material in the sample, so it does not show the amount of solid material lost during the decomposition.

The specific density of peat (closely correlated to the components of the plant residues in it) is relatively low, usually between 1.0 and 1.6 kg/m³. Also the bulk density is low, typically ranging from 0.1 to 0.5 Mg/m³ (Jinming and Xuehui, 2009).

About the elemental composition, the five basic elements of peat are C, H, N, O and S. The proportion of them depends on the degree of decomposition; generally, the carbon and hydrogen content (that are the most important elements for its use as a fuel) increase during decomposition, while oxygen and hydrogen decrease (see

Table 4.6 in § 4.1.4). Simplifying further, peat is composed of an organic material and an inorganic material (principally ashes).

According to the book of Jinming and Xuehui (2009), the organic components of peat can be divided into the following four groups (Table 1.1):

- bitumen, the organic matter which dissolves in hot organic solvents;
- water-soluble, easily hydrolysable substances and cellulose; their contents decrease with the increment of the decomposition degree of the peat;
- humus, including humic acid and fulvic acid;
- all the components that do not hydrolyse in water, like lignin, lignin-like matter, cutin, suberin...

Table 1.1 *Principal group components in peat, their composition and their structures (Hörnell, 2001).*

COMPONENT	TYPICAL CHEMICAL COMPOUNDS AND/OR STRUCTURES IN PEAT COMPONENTS
Bitumen (B)	Waxes, resins (acids, alcohols, polymeric products, terpenes), paraffins and sterols; High concentration of -CH ₂ structural units
Humic acids (HA)	Condensed aromatic, hydroaromatic and heterocyclic structures; Functional groups in decreasing order of content: carboxyl, carbonyl, phenolic hydroxyl, alcoholic hydroxyl
Nonhydrolysables (NH)	Three-dimensional polymer of phenylpropane units; Functional groups: carboxyl, methoxyl, alcoholic hydroxyl, phenolic hydroxyl, carbonyl
Water solubles and easily hydrolysables (WSEH)	Hemicelluloses, glycosides, pectins; Polysaccharides built up of different hexoses, pentoses, and uronic acids
Fulvic acids (FA)	Extracted along with HA (with NaOH) and not precipitated on acidification; FA contain less C and more H than do HA
Cellulose (Cell)	Polysaccharide, polymer of glucose

The major elements (90% of the total) in the ash (the residue of peat after combustion) are Si, Al, Fe, Ca, Mg, Na and P. It is also possible to find 40 other microelements (not more than 1%) and some rare elements.

Under natural conditions, peat is composed of liquid, gaseous, and solid state matter.

The mineral matter contains the original ash (material that was formed by the decomposition of plant debris) and the secondary ash (material that was carried into peat by running water and wind during the accumulation process). The sum of them gives the total ash of the peat.

The water content is high (due of its excellent absorption capacity), usually ranging between 50 and 70% (but it could be higher). The solid component, instead, can be divided into organic matter and mineral matter. The organic matter is the most important one, and it contains humus (20-70%), which is an organic chemical complex with a complicated structure forming during the decomposition, and plant debris that did not decompose fully.

1.2 Peat as a fuel

Peat was a very good alternative to firewood for cooking and heating in the past but, after the spread of the use of gas and oil, its use started to decrease. Nowadays, in those countries where fossil fuel sources are not available (like in Finland), this material starts again to be used for energy purposes.

Peat has to have specific characteristics to be used as a fuel: first at all, it needs a good decomposition degree. Other things to consider are the sulphur content (even though it is small) and the high moisture content, which sometimes can reach values as 90%.

Humidity influences negatively the amount of energy that it is possible to obtain from the combustion of that material. Due to that, a drying of the peat is necessary before its use as a fuel. In addition of this, a material with a high concentration of water have high costs for transport from the peatland to the plant.

The problem associated to the sulphur is that it can be transformed in sulphuric acid and becomes corrosive and very polluting; however, the percentage of this compound in the peat (0.1-0.4%) is less than in coal and lignite (1-3%), so the costs and the effort for the treatments of the gases is smaller.

In addition to this, the combustion of solid material is always associated to unwanted slag and ash. The problem is that the slags remove a big amount of heat that decrease the thermal yield of the furnaces. Therefore, they can provoke encrustations and dirty deposits in pipes and on the walls of the furnaces. Usually, peats with a large content of mineral soil have a high ash value: this one should not be higher than 7 % to have ash of good quality.

1.2.1 *Types of Peat Fuel*

Peat generally has a powder aspect, with more or less amount of fibrous material in it, so it is shaped in different forms to be handled more easily. The principal ones are ⁽²⁾:

- Sod peat: clods of peat that are cut by hand or by machine, and dried in the air. This type of peat is mostly used as a household fuel (sample A and D used in § 4.1 are in this group).
- Milled peat: granulated peat that is produced on a large scale by special machines; it is used as a fuel for power station, or as raw material for briquettes (sample B and C used in § 4.1 are in this group).
- Peat briquettes: small blocks of dried, highly compressed peat that are mainly used as a household fuel.

The milled peat dominates in extraction and consumption (according to Rämö, 2013, its share is 93%).

1.2.2 *Fuel Peat Industry in Finland*

In Finland peat is mainly used in CHP (combined heat and power) plants, where electric energy and heating are produced together. This integrated energy system is very convenient because it requires less fuel to produce a given energy output (reducing the air pollution and greenhouse emissions, too) and provides high-quality energy.

The total number of power plants in Finland is about 60 (where about 27 are industrial plants); the total boiler capacity is 7 200 MWth in total (Paappanen et al., 2005). Typically these plants produce two-thirds heat and one-third electricity, utilizing mainly a fluidized-bed boiler.

There are three groups of producers: the first one is Vapo Oy Energy, a state-owned company with the largest peat production area (around 50 500 hectares). Another big company is Turveruukki Oy, situated in the city of Oulu, with a production area of 6 900 hectares. Both of them own vary heat and power plants and produce material to use as domestic biofuels.

The third group is represented by small-scale producers (around 100 units with 7 600 hectares as peat production area), that have established combinations by which they secure the fuel supply to large power plants.

² <http://www.peatsociety.org/peatlands-and-peat/peat-energy-resource>

1.3 Motivation and objectives

As Finland is a big peat source, the interested is to find an alternative way to use it in energy production, beside combustion. Pyrolysis is a process that gives different products depending on the operating conditions: the amounts and the characteristics of the solids (char or coke), the liquid product (tar) and of the gases vary with the variation of parameters as temperature, heating rate, particle size, residence time, etc.

This Thesis is intended to analyse the yield of production of the solid product and its characteristics (the carbon content in particular) at different temperatures and residence times of pyrolysis from some peat samples, in order to see which are the best conditions to obtain coke suitable for other processes. In addition, there is a section where the initial peat samples are studied and categorized to define the properties of different kind of raw materials.

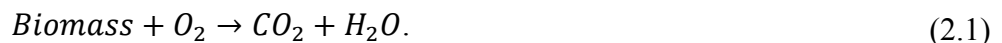
Chapter 2

Combustion, Gasification, Pyrolysis of Biomasses

In the last years, with the rising of price and the diminishing of reserves (petroleum, coal and natural gas), biomasses have been seen as a more sustainable and “green” alternative to the common fossil fuels. This interest increases in countries where there are not domestic reserves of either coal or petroleum but there are significant forest resources, like Finland.

Nowadays biomass can be transformed through thermochemical process to produce steam that it is necessary to activate an engine for the production of electricity, or to obtain useful chemical compounds (like syngas or methane).

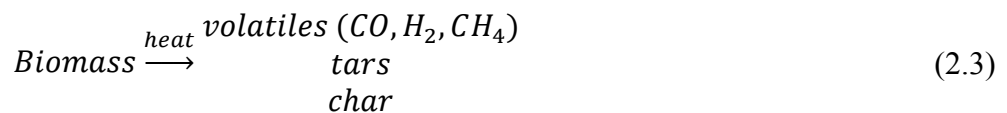
In base of the amount of air provided, the chemical process are mainly divided in combustion, gasification and pyrolysis. Combustion is done in excess of oxygen (respect of the stoichiometric amount for the complete oxidation) and it is described by the following reaction:



Gasification, instead, is done in shortage of oxygen; its reaction is:



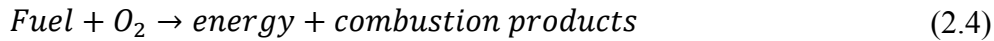
while pyrolysis (done in absence of oxygen) is described by the following reaction.



The products obtained depend on vary factors, as the reaction conditions (temperature, residence time...), the kind of biomass, the type of reactor, etc.

2.1 Combustion

Combustion is an oxidation exothermic reaction between a fuel and a combusive agent (oxygen in most of the cases).



In the ideal case, this process is the complete oxidation in carbon dioxide and water.



The complete oxidation releases a certain amount of thermal energy, gases and ashes. These amounts (respect on the initial mass of the fuel) depend on the chemical and physical characteristics of the material.

For biomass, the combustion is composed in three principal phases:

- **Drying:** the water contained in the material evaporates and, after that, the biomass is heated until it reaches the pyrolysis threshold. In this phase, the moisture content of the fuel is very important because water absorbs some energy released during the combustion process.
- **Pyrolysis/gasification:** the biomass is degraded in char in absence or partial absence of oxygen and its volatiles leave the solid material.
- **Oxidation of the char and combustible gases.**

These three steps are ideally sequential only in a single molecule level, but in reality they occur simultaneously on the bed where the biomass is burning.

Concerning the peat, for many years (especially in Finland) it was burned to obtain heat (as it has been said in § 1.2.2), but nowadays it has been discovered that burning it together with the wood is very convenient. Indeed, due to its mineral content, peat helps controlling the combustion process and reduces the corrosion in the superheated tubes (³); in addition, the SO₂ emissions are lower.

As is possible to see in Figure 2.1, in Finland around 60 power plants (mostly CHP) and more than 120 heat boiler plants use peat together with wood-based fuels (excluding small heat boilers in individual farms etc.) (Rämö, 2013).

³ <http://www.peatsociety.org/peatlands-and-peat/peat-energy-resource>

Most of the combustion plants in Finland are using fluidized bed furnaces, a technology that permits to maximize the surface of the biomass exposed to the combustive air. The reaction occurs inside a suspension of inert granular material (silica sand for instance) that is maintained in agitation by air or gas blown from the bottom of the furnace.

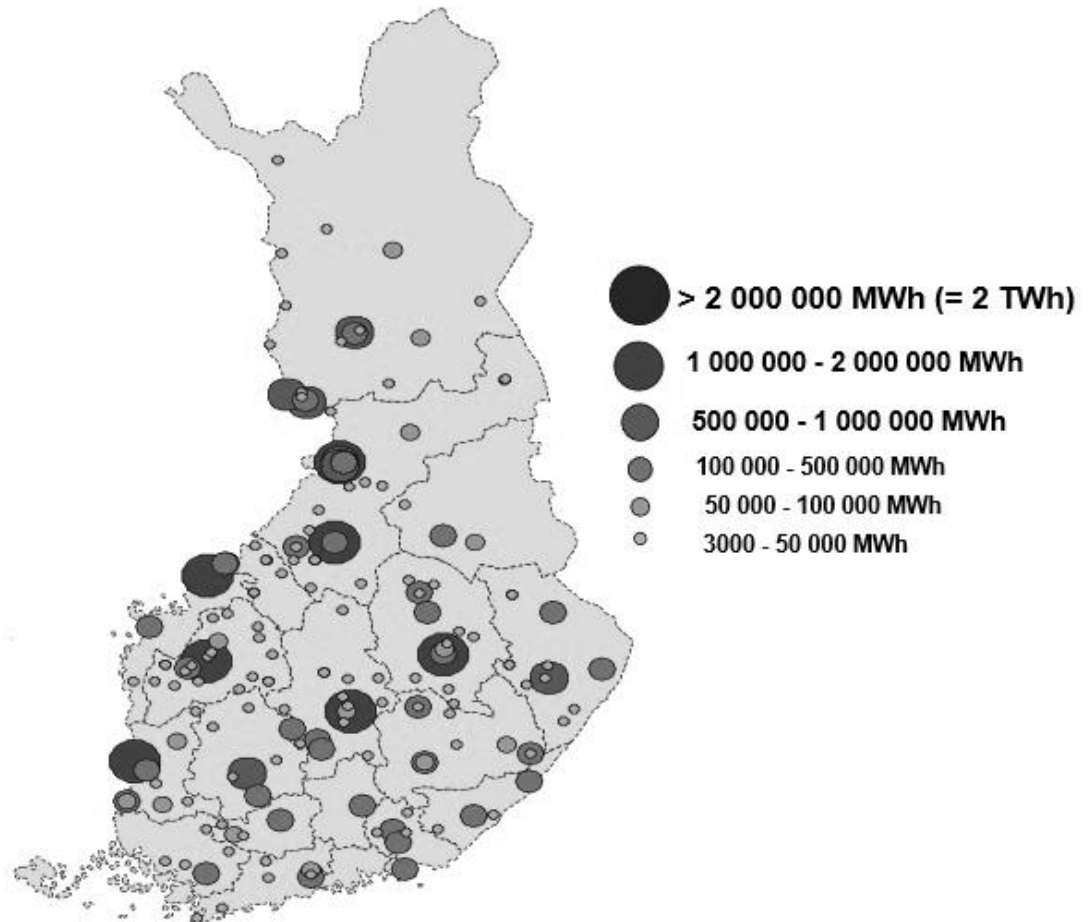


Figure 2.1. Power plants and boilers fuelled by peat (Rämö, 2013).

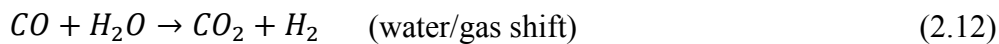
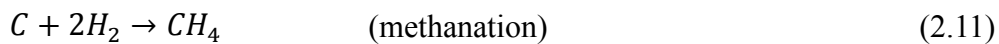
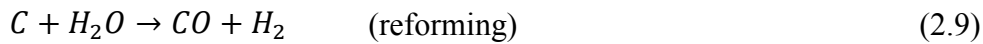
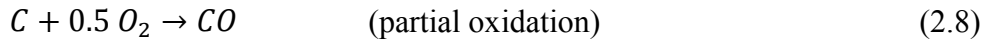
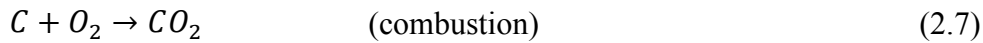
2.2 Gasification

Gasification is a partial oxidation of a material (liquid or solid) with a temperature range between 800 and 1 100°C. In this case, the amount of air (or oxygen) provided is less than the stoichiometric one.

The gasification agent can be air, oxygen or steam. The utilization of air is the less expensive choice, but the gas produced has a low heating value because it is very diluted in nitrogen. This problem can be partially solved by using oxygen and obtaining a vector with a medium heating value. However, the best results are

found with steam: it is cheaper than the previous one, and the gas obtained has a bigger heating value, but in this case the process becomes endothermic.

There are vary reactions that occur in gasification:



The products of the gasification are:

- gases with a medium-low heating value (4-15 MJ/Nm³), composed by CO, H₂, CO₂, CH₄;
- tar, a fraction composed by heavy hydrocarbons that are condensable at room temperature;
- char, that is the inert fraction of the initial material.

The most interesting product is the syngas, a mixture of CO and H₂ that can be utilised in different ways. Indeed, it can be directly combusted in furnaces (because it does not need any purification, so it can be used for heating production), or in units (like internal combustion engines) for the electricity production. In this case, a pre-treatment of the gas has to be done to eliminate particulates and condensable fractions to avoid eventual problems in all the processes after the gasification. Another important utilisation of the syngas is as raw material for important chemical reactions, like the synthesis of hydrogen.

Related to peat, the biggest problems encountered in gasification is its high moisture content (it will be more exhaustively discussed in § 4.1.1), because it provokes a diminishing of thermal efficiency (as in combustion), and of heating values of the gas. Also its ash content can be an issue: slagging or clinker formation in the reactor are typical problems causes by ashes. These problems can partially be solved with drying and a careful selection of the starting material: in Finland, sod peat of approximately 30-40% moisture content is used to feed updraft gasifiers (or counter current gasifiers, Figure 2.2 (a)), while fairly dry peat-pellets are used in downdraft gasifiers (co-current gasifiers, Figure 2.2 (b)) for gas-engine applications (FAO, 1986).

In the updraft gasifier, the biomass is introduced from the top, while the air is blown from the bottom, under the retaining grid. The char (that is the biomass without the volatiles) is subjected to a partial oxidation (with $T > 1\,000^{\circ}\text{C}$) in the combustion area; the formed ashes fall through the grid and the volatiles (released in the pyrolysis section) go to the top of the reactor transferring heat to the reduction area, where the principal constituents of the syngas are produced.

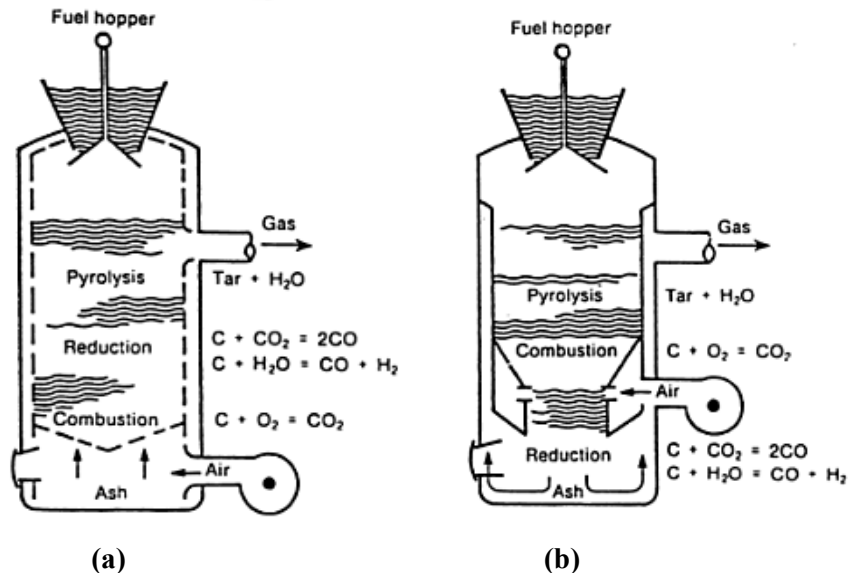


Figure 2.2. Schematic diagram of and updraft (a) and downdraft (b) gasifier showing reactions occurring in each zone. (Reed et al., 1988)

In the downdraft gasifier, instead, the synthesis gas goes from the top to the bottom of the reactor, so it goes to the same direction of the one of the solid fuel. In this case, the combustion is situated in a restriction to create a compact area with high temperature where the pyrolysis gases can pass and tar cracking occurs. It is in this section, indeed, that the air is introduced; the reduction area is between the restriction and the supporting grid. This configuration solves the problem of tar entrainment, but adds the problem of obstruction of the restriction (due of that, the particles of the biomass have to be small); plus, the biomass has to have a low moisture content.

2.3 Pyrolysis

The pyrolysis is a thermochemical decomposition process of biomass obtained by heating in absence of oxidant elements, at temperatures between 400 and 800°C .

In general, the decomposition degree of the biomass during this process depends on some characteristic parameters:

- temperature of the reaction;
- heating rate of the biomass;
- residence time of the material inside the reactor;
- size and shape of the biomass;
- possible presence of catalysts.

The type and the yield of products obtained depend on these factors and the initial composition of the biomass. Physically, the products are:

- a gaseous fraction with a medium-low heating value that contains CO, CO₂, hydrocarbons (CH₄, C₂H₄, C₃H₆), H₂O, H₂;
- a liquid oil fraction that contains tar, water and organic compounds with low molecular weight as aldehydes, acids, chitons, alcohols;
- a solid product composed by residues with a higher molecular weight as carbonaceous portions, ashes, inerts and metallic species.

The pyrolysis process and its features are further analysed in § Chapter 3. In general, an increase of the temperature causes an increase of the gases produced; this is an effect of the winning of de-volatilising reactions on the charring reactions (which are more frequently at low thermal regimes). The liquid fraction, instead, has a maximum in production at nearly 500°C with cooling times of 0.5 and 2 seconds.

About the residence times of the organic substance in the reactor, they have to be high if the interest is to produce char or gases. If the aim is to produce tars (that is the liquid fraction), small residence times and a high heating rate (between 10 and 200°C/s) are required.

The products are used for different purposes. In general, char is utilised in furnaces, while gases are used in heating or steam production. Tar is considered the most interesting product from an energetic point of view, because it is very similar to petroleum, but it has some defects: it is not very stable, because it contains vary oxygenated groups; it is expensive to obtain and some high-value compounds contained in it are difficult to extract.

2.3.1 Peat Pyrolysis: Literature Review

Regarding to pyrolysis of biomasses, a lot of work has been done in the past years, but not specifically about peat pyrolysis. Probably the reason of this is the uncertainty of the renewability of peat (the definition of “biomass” and the positioning of peat in this class will be shortly discussed in § Chapter 3). Above at all, the main problem is that most of the studies analyse the gaseous products and/or the liquid product (not the solids). In this section, it is reported the main works that have been made on peat char after pyrolysis.

One of the most extended paper on the study of peat is by Fuchsman (1980). The pyrolysis process is described from the preliminary operations (like the selection of the most suitable material) to the detailed analysis of the three products (chars, tars and gases). He reports that, at low-temperature coking (500°C), the yields of coke expected are 30-40% for Swedish peat and 32.4% for German peat. He described the dependence of this yield on heating rate too: if the peat is heated too rapidly, some reactive low-molecular-weight fragments may be volatilized before they can react in the condensed phase to form high-molecular-weight substances, and the coke yield decreases. The reason is that it is more probable to carbonize these high-molecular-weight substances than to volatilize them.

The properties of the char have been studied by Sjöström and Guanxing (1990) too. In this case, a pressurized rapid pyrolysis in a free-fall tubular reactor has been carried on, with a collection of the char at the bottom of the equipment. Their work was mainly about the char reactivity, at different times and temperatures, after a rapid heating at elevated pressure, for a further gasification. The most interesting thing in this text for the aim of this project is that this rapid heating of peat (and, more generally, of biomass) increases the gas and tar yields at the expense of char. Furthermore, the contact between tars and char reduces the rate of the steam-char reactions that happen in a consecutive gasification. These observations have to be taken in account if the aim of the char production is to utilize them in other processes.

In the work of Sutcu (2007) all the three products were studied after a pyrolysis in a fixed-bed tube furnace in various conditions. The study shows that the yield decreases with the increasing of pyrolysis temperature (more specifically from 51.44% to 36.19%). Increasing the heating rate, these values decrease again (due to the increase of the speed of the volatiles to leave the peat), as it has been said by Fuchsman (2012) before.

A different methodology to study the char has been used by Aho et al. (1989). They decided to use Fourier transform infrared spectroscopy to study the peat pyrolysis. The main advantage is the possibility of studying the variation on the composition of the char at different charring temperatures, by the observation of the intensity of the signals and the changes in the sample weight. The final result is an estimation of when the degradation reactions for the main components of peat occur.

The main documentation about the pyrolysis of peat has been made, however, by Roy et al. (1983). This work is a general review of many studies made by different authors and it detailing describes the products, the reaction mechanism and their parameters, together with a study on some catalytic effects and suggestion for industrial application. In § 3.3 there will be many references to this paper.

Another different group of experiments are called analytical pyrolysis. The purpose of those is to provide analytical information on the initial sample, and not just the transformation of it into other compounds. The study in this Thesis is not attributable to this methodology (because the aim is to study a char produced, not the starting peat); however, the work of Moldoveanu (1998) is a good reference if the purpose is to classify the initial peat.

Chapter 3

Peat Pyrolysis

Pyrolysis is a thermal decomposition of carbonaceous materials in the absence of oxygen and it is used in thermochemical technologies to convert biomass into solid, liquid and gas products for use as an energy source. In this chapter its principal features are described.

3.1 Introduction

In general, biomass decomposes to generate vapours, aerosols, and some charcoal-like char. The gaseous/vapour phase is then cooled and condensed, and a dark brown mobile liquid is obtained (called tar or bio-oil), with a heating value that is about half of that of conventional fuel oil. Both tar and solid char can be used as a fuel, while the gas can be recycled back into the process so that the total production of waste is theoretically equal to zero.

It is important to understand the difference between pyrolysis and gasification. This latter decomposes biomass to syngas by controlling the amount of oxygen inserted, while pyrolysis is done in absence of oxygen, and it is more related to carbonization (where the principal product is solid char), or to processes in which oils are the preferred products.

In general, pyrolysis causes the following changes (Mohan et al., 2006):

1. heat transfer from a heat source, to increase the temperature inside the fuel;
2. the initiation of primary pyrolysis reactions at this higher temperature releases volatiles and forms char;
3. the flow of hot volatiles toward cooler solids results in heat transfer between hot volatiles and cooler unpyrolysed fuel;
4. condensation of some of the volatiles in the cooler parts of the fuel, followed by secondary reactions (that can produce tar);
5. autocatalytic secondary pyrolysis reactions proceed while primary pyrolysis reactions simultaneously occur in competition.

Further thermal decomposition, reforming, water gas shift reactions, recombination of radicals, and dehydrations can also occur, which are a function of the residence time/temperature/pressure profile of the process. The effect of these parameters in the main products are further described in § 3.3.1.

3.2 Pyrolysis Products

The pyrolysis products can be very different depending on the raw material composition, the particle size, the heating rate and the final temperature. According to Roy et al. (1983), the main products of peat pyrolysis are:

- coke or semi-coke (depending on the degree of carbonization), a solid carbonaceous residue. This product has different denominations: generally it is called char (as in this work); the “semi-coke” denomination is used when the heating temperature reached is about 550°C, or when the volatile matter content in the material is relatively high. The term “peat coke”, instead, is used when the pyrolysis undergo at about 900°C. The composition of it depends on many factors, as the original composition of the peat or the process followed; some indicative values of the elementary composition after a low-temperature decomposition of peat are 84-88% C, 2-3.5% H, 5-9% O and 2-4% N, and a calorific value of 7 300 - 8 200 kcal/kg of organic matter.
- peat tar, a liquid distillate consisting of a viscous organic phase. This one is considered the most interesting product for many researches (it is physically very similar to petroleum, but more unstable). It is a dark-brown to almost black, strong-smelling product, which at room temperature is a semi-solid or viscous liquid. Also in this case, an indication of the elementary composition is 72.0% C, 9.4% H, 3.8% N and 14.8% O, and the calorific value is about 8 800-9 500 kcal/kg. The type of pyrolysis affects greatly the quality of the final tar: a high-temperature pyrolysis provokes a degradation of the liquid product.
- an aqueous phase that usually contains acetic acid, methanol and other low-molecular weight polar organic substances;
- non-condensable pyrolysis gas.

The attention in this work is on the char: the main aim is to study the yield and the composition of them at different temperatures and residence times (see § Chapter 4), so the tars and the gases will not be examined.

3.3 Pyrolysis Principles

The main pyrolysis reaction is simply described by the next formula:



Depending on the operating conditions, the pyrolysis process can be divided in 4 subclasses: slow pyrolysis, conventional pyrolysis (under slow heating rate), fast pyrolysis and flash pyrolysis (if the aim is the production of mainly liquid and gaseous products) (Table 3.1).

Table 3.1. Mass percentages of the products for each type of pyrolysis. (Daniele Dell'Antonia. Lecture about "Energie rinnovabili. Tecnologia e impiantistica per l'utilizzo delle colture", 2012-2013).

	LIQUID	CHAR	GASES
FAST PYROLYSIS			
Moderate temperature (~500°C) Short hot vapour residence time (< 2s)	75% 25% water	12%	13%
INTERMEDIATE PYROLYSIS			
Low-moderate temperature Moderate hot vapour residence times	50% 50% water	25%	25%
SLOW PYROLYSIS			
Low-moderate temperature Long residence times	30% 70% water	35%	35%
GASIFICATION			
High temperature (>800°C) Long vapour residence times	5% tars	10%	85%

The slow pyrolysis is a process characterised by:

- very low reaction temperature (between 300 and 500°C);
- a limited heating rate of the biomass;
- very long residence time in absence of oxygen;
- production of big amounts of char (almost 35% of the initial biomass).

The principal features of the conventional pyrolysis, instead, are:

- moderate heating rate (20°C/s);
- reaction temperature below to 600°C;
- residence time between 10 seconds and 10 minutes;
- production of almost equal amounts of char, gases and tars.

The fast pyrolysis is designed to obtain big amounts of tar (until 80% of the initial organic material). To do that, these indications have to be satisfied:

- temperatures around 500°C;
- short contact times (typically below 2 seconds);
- the particles of the biomass have to reach the optimal temperature very quickly;
- the exposition of the biomass to medium heating regimes has to be as small as possible (to avoid the formation of char).

Latest, the aim of the flash pyrolysis is to release big amounts of gases (CO, H₂, CO₂), that can be eventually cooled and condensed. The temperatures are higher than 650°C and the contact times are smaller than a second, so it is faster than the fast pyrolysis.

3.3.1 *Pyrolysis parameters*

As was already said in § 2.3 , there are many parameters that change the products and the reactions in a pyrolysis process: in this section, the effect of temperature, peat pre-treatment (“bertinization”), contact time and size of the particles, heating rate and pressure will be shortly described (the following information are taken from the review made by Roy et al., 1983).

3.3.1.1 Temperature

The range of temperature where the pyrolysis is conducted influences the final product: in a conventional slow pyrolysis, the formation of tar starts at about 170-200°C, reaching a maximum between 250-500°C, and then starts to decrease. The yields of solids, instead, decreases with an increase of temperature between 250 and 500°C.

This final value reached and the original type of peat affect the composition of the final coke: for instance, in a temperature range from 350 to 500°C the abrasability of the char decreases while the strength of the char increases (this one is very influenced by the initial moisture content of peat too).

3.3.1.2 Heat pre-treatment

Usually, in order to obtain more valuable products, a preliminary heat pre-treatment of peat at low temperature is done. This process is called bertinization, it is conducted under fast pyrolysis conditions and it eliminates most of the oxygen content before to proceed with the secondary pyrolysis of the solid residue

(called “bertinate”) at higher temperatures. The optimum temperature range for it is between 250 and 400°C: this permits to obtain good quality coke with higher yields.

3.3.1.3 Contact time

The contact times of the original peat particles and of the products are important because they may provoke secondary reactions as re-condensation, re-polymerization or secondary cracking. Two factors that influence these reactions are the heating rate (because re-condensation is more probable under slow-heating rate conditions) and the partial pressures of gases and vapours (that greatly affect the number of gas-phase collisions).

Starting from a bertinate, Roy et al. (1983) reported that the yields of coke increase by increasing the contact times, while an opposite effect is registered if raw peat is utilised (this is a further evidence of heat pre-treatment importance).

The contact time is also the parameter that distinguish the type of pyrolysis: if it is lower than 0.1s, it is called fast pyrolysis; otherwise it is called slow pyrolysis.

3.3.1.4 Heating rate

The heating rate of the feedstock is taken in account mainly in slow pyrolysis, because in fast pyrolysis it is assumed that the peat reaches the wanted temperature almost instantaneously (and the main parameter remains the contact time).

In fast pyrolysis conditions, however, low heating rates provokes a reduction in the liberation of volatiles (above at all between 200 and 400°C), and an increase of the carbon content in the char.

3.3.1.5 Pressure

The effect of the partial pressures of the vapours is described in the contact time section (§ 3.3.1.3); in this part the total pressure in the system is taken in account. In a laboratory scale, working under reduce pressure (≤ 10 mmHg) permits to obtain higher yield of tar than working in atmospheric pressure, but lower yields of other products. These yield differences, however, are less evident in an industrial scale than in a laboratory scale.

An important result is that the calorific value of the char at reduce pressure is lower than the one at atmospheric pressure (both in laboratory and industrial scale).

3.3.1.6 Particle size

The product yields are affected by the dimension of the particles of the peat. Indeed, by increasing the particle size from 0.05 mm to 2.0 mm, the yield of tar increases from 2.7% to 7.8%, the yield of gases from 54.8% to 43.3% and the yield of coke by 4%. In particular, the coke yield increased sharply from a particle size range of 0.1-0.2 mm to 0.2-0.4 mm.

3.3.2 The degradation of cellulose, hemicellulose, lignin in pyrolysis

For a generic biomass, composed of hemicelluloses, celluloses, lignin and minor amounts of extractives, the pyrolysis has different rates and mechanisms depending on the amount and the type of these components. Usually, the thermal degradation of hemicellulose is the first one that happens (temperatures of 470-530 K), followed by cellulose (510-620 K) and lignin (550-770 K) (Demirbas and Arin, 2002).

Peat, however, is not a biomass as commonly defined (“biological material derived from living, or recently living, organism”⁴), because is an intermediate stage between plant residues and coal, and if the degree of decomposition is very high, it will be more similar to a fossil fuel. So, in pyrolysis the degree of humification plays an important role: a peat with a low decomposition (containing like 70-80% of carbohydrates) will give low amounts of coke and tar as products, and high yield of water. This behaviour is similar to the carbonization of cellulose and related carbohydrates: it means that the pyrolysis of little decomposed peat can be correlated to the one of a generic biomass. A different situation can be found in highly decomposed peat: they contain only 50-60% of humic matter, plus small amounts of bitumen, carbohydrates and other components. According to Fuchsman (1980), if the amount of bitumen is very big, the tar yield will be very high, while peat humic acids give high yields of semi-coke.

In this work, the interest is to have high yield of coke from the pyrolysis: the ideal case is to have highly decomposed peat, with a big amount of humic acids.

In addition of this, if the peat is very old, it contains less cellulose and hemicellulose than a newer one. Therefore, it does not contain lignin, but it has substances that are chemically and functionally similar to it. Lignin, indeed, is

⁴ <http://www.biomassesenergycentre.org.uk>

relatively stable during humification, and it is regarded as a precursor of humic acids of peat. So it has been considered that the lignin is “transformed” in humic acids during decomposition: a proof is that the fungi, which degrade lignin, are not normally found in peat.

However, the degradation of cellulose, hemicellulose and lignin are reported in the subsequent paragraph, even if the amounts of these compounds are very small, because it can be supposed that the organic constituents of peat have a similar behaviour.

The rate of the decomposition depends on many factors, like composition of the raw material, reactor type, temperature, particle size, heating rate and pressure. The thermal degradation properties, anyway, can be summarized in the following way:

Thermal degradation of hemicelluloses > of cellulose > of lignin.

The cellulose starts to decompose at nearly 240-350 °C, generating gas composed of 90-95% CO₂ and 5-10% H₂O (by volume). At low temperatures, the main reactions are the elimination of water, CO and CO₂, and they are the major products together with char.

Non-cellulosic carbohydrates, instead, begin to be thermally degraded at lower temperatures than cellulose, but they follow the same pyrolysis mechanism. Hemicellulose decomposes at temperatures of 200-260°C, giving rise to more volatiles, less tars, and less chars than cellulose.

About the lignin pyrolysis, at low heating rates, the composition of the product is 50% char yield (by weight), 15-20% of tars and an aqueous distillate composed on water, methanol, acetic acid, acetone and acetaldehyde. Lignin is more difficult to dehydrate than cellulose or hemicellulose: it usually decomposes at 280-500 °C.

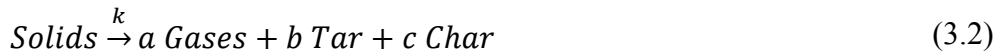
However, the rate of thermal degradation of lignin is very slow below 200 °C, and the reaction products are influenced by the method of isolation of lignin. Above 300 °C, instead, these problems are not noticed: therefore, the yield of char decrease, while the formation of condensable products is more probable.

3.4 Pyrolysis reactions and mass balances

Different models are proposed to explain the pyrolysis reaction of biomasses (Prakash and Karunanithi, 2008).

The simplest ones are the one step global models: only the primary reactions are taken in account, so the peat is decomposed just in volatiles and cokes.

This model is used later in § 4.3 . The pyrolysis reaction is simply described by the following mechanism:



where k is the kinetic constant of the reaction and a, b, c are the yield coefficients of the different products of pyrolysis. The constant k can be expressed by the Arrhenius equation:

$$k = A e^{\frac{-E_a}{RT}} \quad (3.3)$$

where A is the pre-exponential factor, E_a is the activation energy, R is the gas constant and T is the temperature of the reaction.

So, the mass balances of the reactant and of the products are:

$$\frac{dm_{solids}}{dt} = -k \cdot m_{solids} \quad (3.4)$$

$$\frac{dm_{gases}}{dt} = a \cdot k \cdot m_{solids} \quad (3.5)$$

$$\frac{dm_{tar}}{dt} = b \cdot k \cdot m_{solids} \quad (3.6)$$

$$\frac{dm_{char}}{dt} = c \cdot k \cdot m_{solids} \quad (3.7)$$

Another group of models takes in consideration the secondary tar cracking, as it is done in the work of Tanoue et al. (2007), where the pyrolysis reactions can be reduced to the one in Figure 3.1 (Broido-Shafizadeh mechanism).

In the primary reactions, the biomass (in this case, the peat) decomposed to gas, tar and char, while in the secondary reactions the tar is further decomposes to light gas and char in exothermic reactions. This model (more accurate, because it takes in account the secondary cracking) is not used in this Thesis because there are not any information about the formed tar and gases: it is not possible to distinguish gases produced in the primary reaction from the ones produces in the secondary reaction. For this reason, the simplest model is further used.

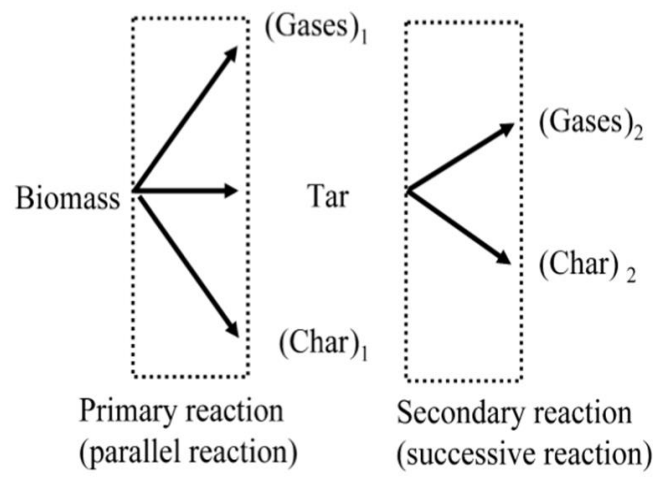


Figure 3.1. *Pyrolysis reaction mechanism (model with secondary tar cracking) (Tanoue et al., 2007).*

Chapter 4

Experiments

In this chapter the experiments carried out in this project are described with the associated results. They comprise the analysis of the peat available in the university and the pyrolysis done.

4.1 Peat samples

For the experiments in the laboratory, four different samples of peat are used (A, B, C and D) (Figure 4.1), taken from a peatland in Virkasalonneva, in Karvia (about 80 km NE of the town Pori in western Finland, Figure 4.2). In this area 67 mires are covering 8 559 hectares, with 125.83 million m³ of peat contained.

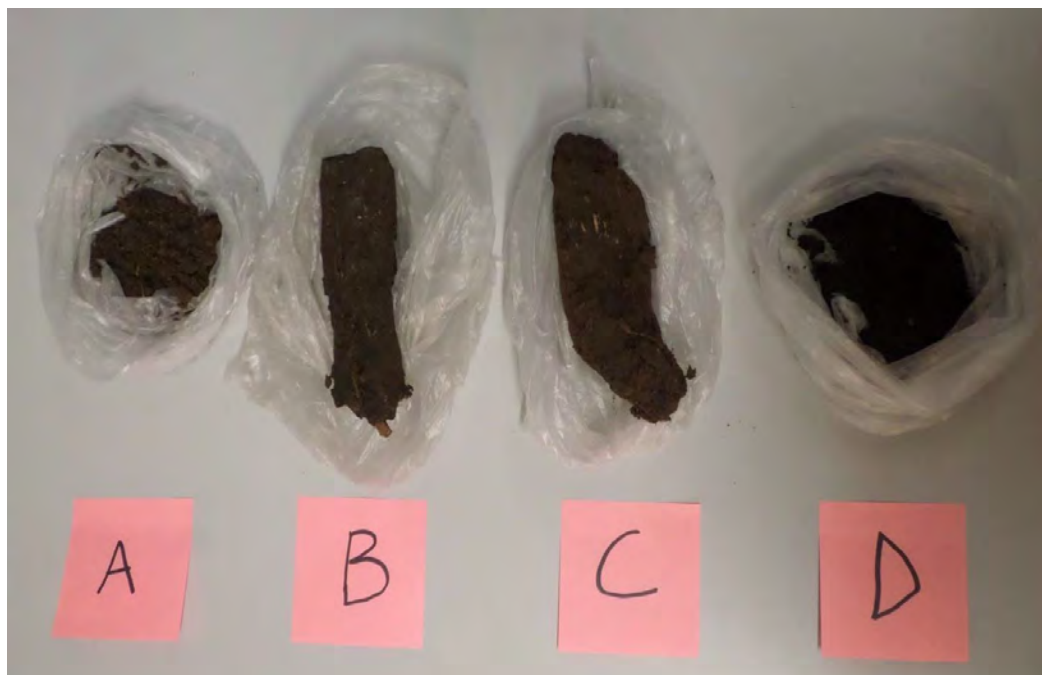


Figure 4.1. *Photograph of the four peat samples.*

The aspect of the samples are very different from each other: samples A and D are like a powder, while samples B and C are like briquettes. The reason is that the samples B and C have been previously pressed in a machine, to be more easily handled and burned in a house furnace. In order to do this, the crude peat has to be

dried before to go in the press; thereby, it is expected that the moisture content of these two samples are lower than the one of A and D.

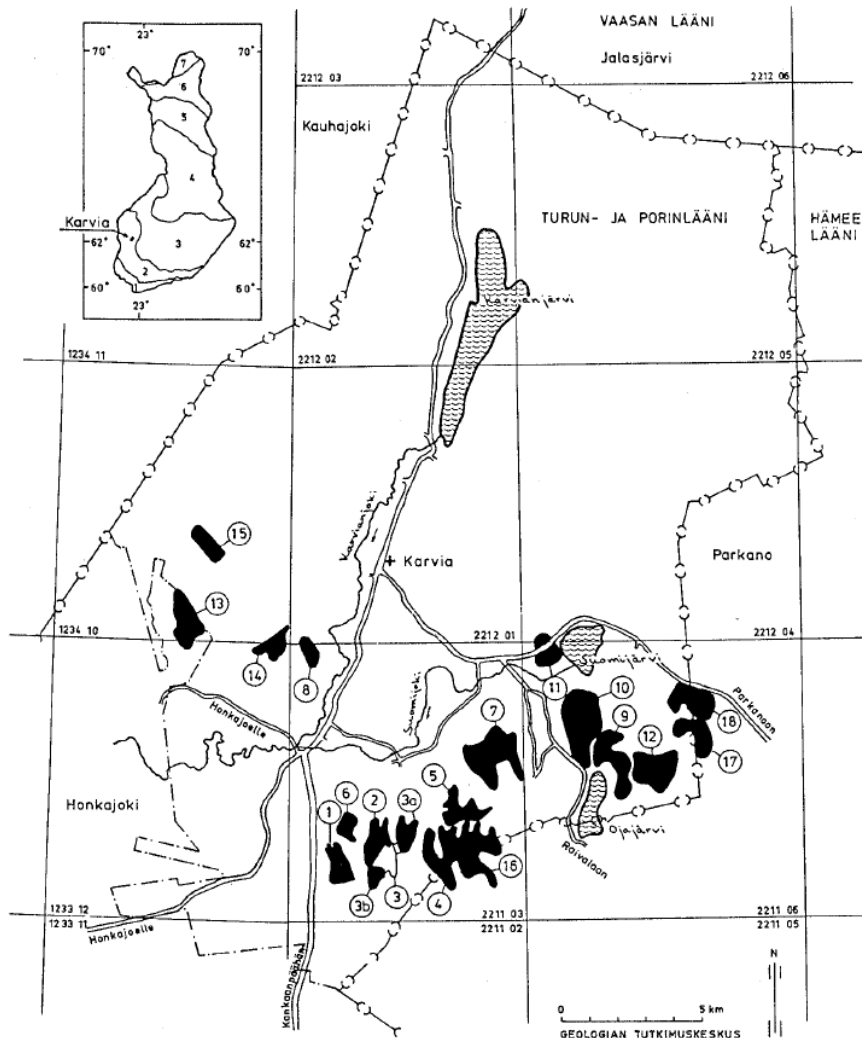


Figure 4.2. Peatlands in Karvia (1= Virkasalonneva). (Stén and Moisanen, 1995)

4.1.1 Moisture content

The moisture content is the percentage of water contained in the sample of peat. To determine this, the sample is weighed before (m_0) and after (m_1) the drying in an oven (temperature: 110 °C) for 30 hours. The weights of the samples are checked during this period, and the drying is stopped when the fluctuations stop.

Then, the moisture content is calculated with the formula:

$$MC = \frac{m_0 - m_1}{m_0} \cdot 100 \quad [\%] \quad (4.1)$$

The results are written in Table 4.1.

Table 4.1. *Moisture content of samples A, B, C, D.*

SAMPLE	A	B	C	D
1 measurement	36.3%	23.4%	29.5%	51.7%
2 measurement	37.5%	24.3%	31.3%	53.4%
Averaged Moisture Content [%]	36.9%	23.9%	30.4%	52.5%

As was expected, the samples B and C are the ones with the lowest moisture content, because they were pressed to be a better fuel.

4.1.2 Heat of combustion

To determine the heat of combustion of each sample of peat, an oxygen bomb calorimeter is used (Figure 4.3). This one measures the heat released during the burning of a sample in an oxygen atmosphere in a close vessel, under controlled conditions. The sample is put into a close vessel, in contact with a wire (to ignite a spark to burn the peat). The oxygen (at 30 bar pressure) is loaded into this, and then the vessel is put in a stirred tank with 2 kg of distillate water, in contact with a detector to monitor the combustion. When the sample is completely burned, the calorimeter gives the corresponding heat of combustion ($\Delta H_{c,measured}$).

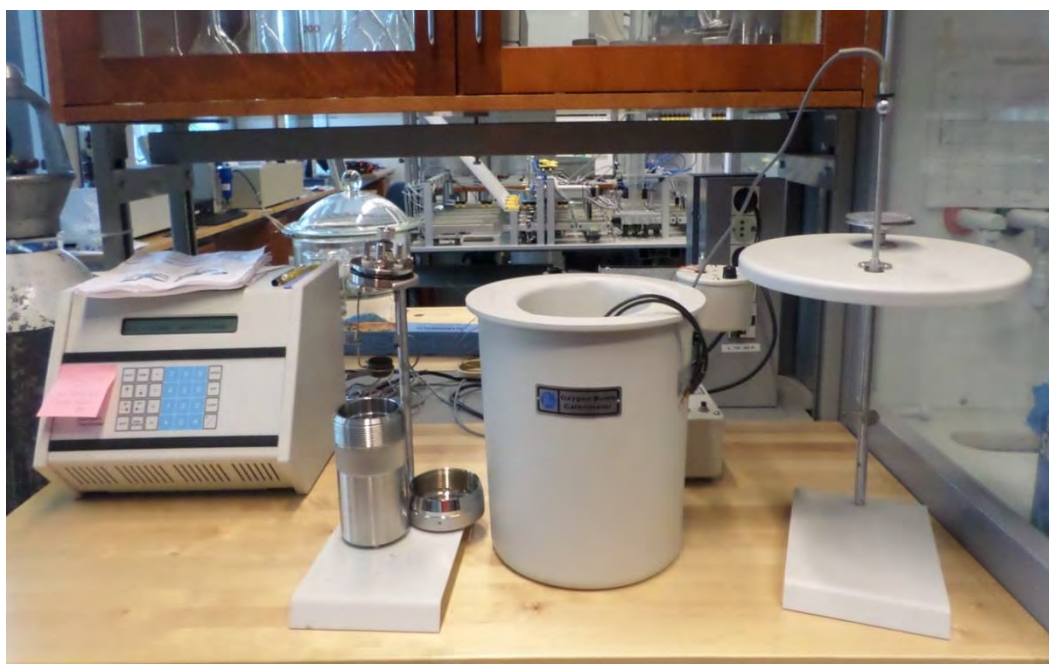


Figure 4.3. *Photograph of the Oxygen Bomb Calorimeter.*

To obtain the heat of combustion on dry basis, the following formula is used:

$$\Delta H_{c,dry} = \frac{\Delta H_{c,measured}}{1 - MC} \quad [\text{MJ/kg}_{dry}] \quad (4.2)$$

where MC is the moisture content of the sample.

The results are written in Table 4.2.

Table 4.2. Heat of combustion of samples A, B, C, D (made with an oxygen bomb calorimeter).

SAMPLE	A	B	C	D
1 measurement	20.36	23.07	20.49	21.66
2 measurement	20.84	23.03	20.46	21.74
Averaged $\Delta H_{c,dry}$ [MJ/kg_{dry}]	20.60	23.05	20.48	21.70

The sample with the highest heat of combustion is B, while the sample with the lowest heat of combustion is C. This is probably due to a different composition of substances in the samples (notice that the values are in dry basis).

4.1.3 Ash content

The ash content in the peat is an important parameter, especially if the main aim is the production of coke. Indeed, the mineral matter (or inorganic content) is not volatilized during pyrolysis, so it remains in the solid products and contaminates the peat coke as ashes.

Peat usually contains a percentage of ash that can vary from 2 to 10 % (Fuchsman, 1980). To measure the ash content in the four samples, the standard ISO 1171 is followed. A little amount of ground peat is weighed (m_1), put in a dry ceramic bowl, and placed in an oven to be burned. First the temperature is increased from room temperature to 500 °C in 60 minutes, then it is increased again to 815 ± 15 °C in 60 minutes, and kept at this temperature for additional 60 minutes. After this amount of time, the bowl is placed in a dryer to cool down, and weighed again (m_2). The ash content is given by the next formula.

$$A_d = \frac{m_2 \cdot 100}{m_1} \cdot \frac{100}{100 - MC} \quad [\%] \quad (4.3)$$

where MC is the moisture content of the peat sample (%). The results are reported in Table 4.3.

Table 4.3. Measurements of the ash content of four peat samples.

SAMPLE	A	B	C	D
1 measurement	5.8%	3.3%	5.1%	4.4%
2 measurement	3.5%	3.1%	4.7%	8.9%
3 measurement	3.2%	3.2%	5.4%	5.7%
Averaged Ash Content [%]	4.2%	3.2%	5.1%	6.3%

As can be seen, the ash content does not exceed 10 % in any of the four samples.

4.1.4 Elemental analysis

The aim of this experiment is to find the elemental composition of the peat, and to try to write an empirical formula for it. To do that, a CHNS Analyzer is used (Figure 4.4).



Figure 4.4. Photograph of the CHNS Analyzer.

This instrument can measure the amount of carbon, hydrogen, nitrogen and sulphur in a sample. The sample is burned in a furnace, and the reaction products pass through a chromatographic column where separation occurs. The result of the

measurement is a chromatograph with a peak for each element found, with an area proportional to the amount of that element in the sample.

Before doing the experiments, it is necessary to calibrate the instrument and to calculate the correcting factors. The first run is done with a standard (in this case sulphanilamide: $C_6H_8N_2O_2S$), whose composition is known (reported in Table 4.4).

When the areas of the peaks are available, it is possible to calculate the correcting factors with the next formula.

$$f_i = \frac{m_{std} \cdot w_i}{A_i} \quad [g] \quad (4.4)$$

where f_i is the correcting factor for the element (in grams), m_{std} is the mass of the sulphanilamide sample used in the experiment (in grams), w_i is the mass fraction of the i th element (from Table 4.4) and A_i is the area of the peak (given by the chromatograph).

Table 4.4. *Chemical composition of Sulphanilamide.*

STANDARD	%
C	41.84%
H	4.68%
N	16.27%
O	18.58%
S	18.62%

Once the correcting factor for each element is known, the correct amount of each element in an unknown sample is given by:

$$m_i = m_1 \cdot w_i = f_i \cdot A_i \quad [g] \quad (4.5)$$

where m_1 is the mass of the unknown sample (in grams).

For each type of peat (A, B, C, D) three different measurements are done. The most delicate phase is the collecting of a meaningful sample from the peat, as it is a heterogeneous solid mixture, with different solids components (like fibrous materials). The elemental analysis needs just few milligrams of the substance, and it should represent the whole mass. To prepare this sample, some grams of material are taken from different positions of the peat piece available, and milled in water with a mixer. Then, the ground solid material is separated from the water

by using under-vacuum filtration, and dried in the oven at 110 °C for 24 hours. After that, it is removed from the filter paper to a small beaker and mixed again. The final sample is taken from this peat powder.

The oxygen content can be calculated by subtracting the mass percentages of ash and the other elements from 100.

$$w_O = 100 - w_C - w_H - w_S - w_N - A_d \quad [\%] \quad (4.6)$$

The results from the NCHS analysis are reported in Table 4.5.

As it is possible to see, at least half of the peat mass is composed of carbon. The content of sulphur is very low (very close to 0.1 %). If these results are compared to the data in

Table 4.6, it can be supposed that the four samples of peat are in the category “Moderately decomposed”.

Table 4.5. Mass percentages of C, H, N, S, O and ash in four peat samples.

Mass percentages				
SAMPLE	A	B	C	D
C	50.26%	55.60%	51.67%	53.49%
H	5.68%	6.30%	5.64%	6.13%
N	1.27%	1.64%	0.94%	1.49%
S	0.13%	0.11%	0.11%	0.10%
O (by difference)	38.01%	33.12%	36.72%	32.16%
ash	4.66%	3.22%	4.92%	6.63%
sum	100.00%	100.00%	100.00%	100.00%

Table 4.6. The most important elements in peat according to the degree of decomposition (percent weight in dry solids). (Source: <http://www.fao.org/docrep/x5872e/x5872e0b.htm#TopOfPage>)

ELEMENT	Degree of decomposition according to Von Post		
	Slightly decomposed	Moderately decomposed	Highly decomposed
C	48-50	53-54	58-60
H	5.5-6.5	5-6	5.0-5.5
N	0.5-1	1-2	1-3
O	38-42	35-40	30-35

4.1.5 Elemental formula of peat

After the determination of the elemental and ash concentration, it is possible to try to find a molecular formula that describes the composition of peat. From the previous measurements, the composition of peat is reported in Table 4.5.

To find the molar percentages, the ash content is excluded; so, the following formula (for example, for the molar percentage of carbon) is used.

$$x_C = \frac{w_C \cdot MW_C}{w_C \cdot MW_C + w_N \cdot MW_N + w_H \cdot MW_H + w_S \cdot MW_S + w_O \cdot MW_O} \quad [\%] \quad (4.7)$$

where MW_i is the molecular weight (in kg/kmol) of the element i (results in Table 4.7).

From these values, the resulting formula of peat is $\text{CH}_{1.341}\text{O}_{0.500}\text{S}_{0.001}\text{N}_{0.022}$. Compared to the coal formula ($\text{CH}_{0.81}\text{O}_{0.08}\text{S}_{0.02}\text{N}_{0.01}$) given by Williams and Larson (2003), peat contains more hydrogen, oxygen and less sulphur.

Table 4.7. Molar percentages of C, H, N, S, and O in four peat samples.

Molar percentages				
SAMPLE	A	B	C	D
C	34.05%	35.41%	35.08%	35.18%
H	45.85%	47.84%	45.64%	48.07%
N	0.74%	0.90%	0.55%	0.84%
S	0.03%	0.03%	0.03%	0.03%
O	19.33%	15.83%	18.71%	15.88%

This means that it contains more water and organic material; if one wants to consider peat as a biomass (described by the general formula $\text{C}_6(\text{H}_2\text{O})_z$), it will be (approximately): $\text{C}_6\text{H}_8\text{O}_3 \sim \text{C}_6(\text{H}_2\text{O})_3$, omitting the low sulphur and nitrogen content. This means that peat contains less water than, for example, cellulose (the principal constituent of biomass, $\text{C}_6(\text{H}_2\text{O})_5$).

These differences influence the heat of combustion of the peat: it is possible to calculate it on ash-free material basis with the following formula (ISO 1928, CEN/TS 14918):

$$\Delta H_{c,bio} = \frac{\Delta H_{c,dry}}{100 - A_d} \quad [\text{MJ/kg}_{bio}] \quad (4.8)$$

The results are reported in Table 4.8.

Table 4.8. Heat of combustion of four peat samples (ash free material).

SAMPLE	A	B	C	D
$\Delta H_{c,dry}$ [MJ/kg _{dry}]	20.60	23.05	20.48	21.70
Ash Content [%]	4.7%	3.2%	4.9%	6.6%
$\Delta H_{c,bio}$ [MJ/kg _{bio}]	21.61	23.82	21.54	23.24

With this value, a comparison between the heats of combustion of different materials can be made (Table 4.9).

Table 4.9. Characteristics of some solid fuels (data for peat measured directly in laboratory; other data taken from the book of Tilmann, 1991).

PARAMETER	FUEL			
	COAL	LIGNITE	WOOD	PEAT
Moisture (wt %)	3.00	33.27	50.00	8.77
Ash (wt %)	10.30	7.25	0.40	4.90
Carbon (wt %)	75.50	44.16	26.15	52.75
Hydrogen (wt %)	4.40	3.28	3.15	5.94
Oxygen (by difference) (wt %)	2.50	10.52	20.25	26.20
Nitrogen (wt %)	1.20	0.77	0.05	1.33
Sulfur (wt %)	3.10	0.75	0.00	0.11
Higher Heating Value (MJ/kg _{bio})	30.82	17.75	10.53	22.55

The amount of water contained in the material influences the heating value: if the moisture content is high (like in wood), the heating value of the biomass is low. As was said before, the amount of water in peat can vary a lot and depends on its surrounding environment, so it is always necessary to dry it before to burn it.

Potentially it is possible to obtain a big amount of energy from burning peat, almost comparable to the one produced by coal.

4.2 Pyrolysis experiment

There are not many examples of a pyrolysis equipment for biomass in laboratory scale; for the experiments, a heated column has been used (Figure 4.5). The sample of peat is inserted from the top in a special chamber; the inlet of the necessary gas for the combustion (in this case, nitrogen) is in the bottom, and it

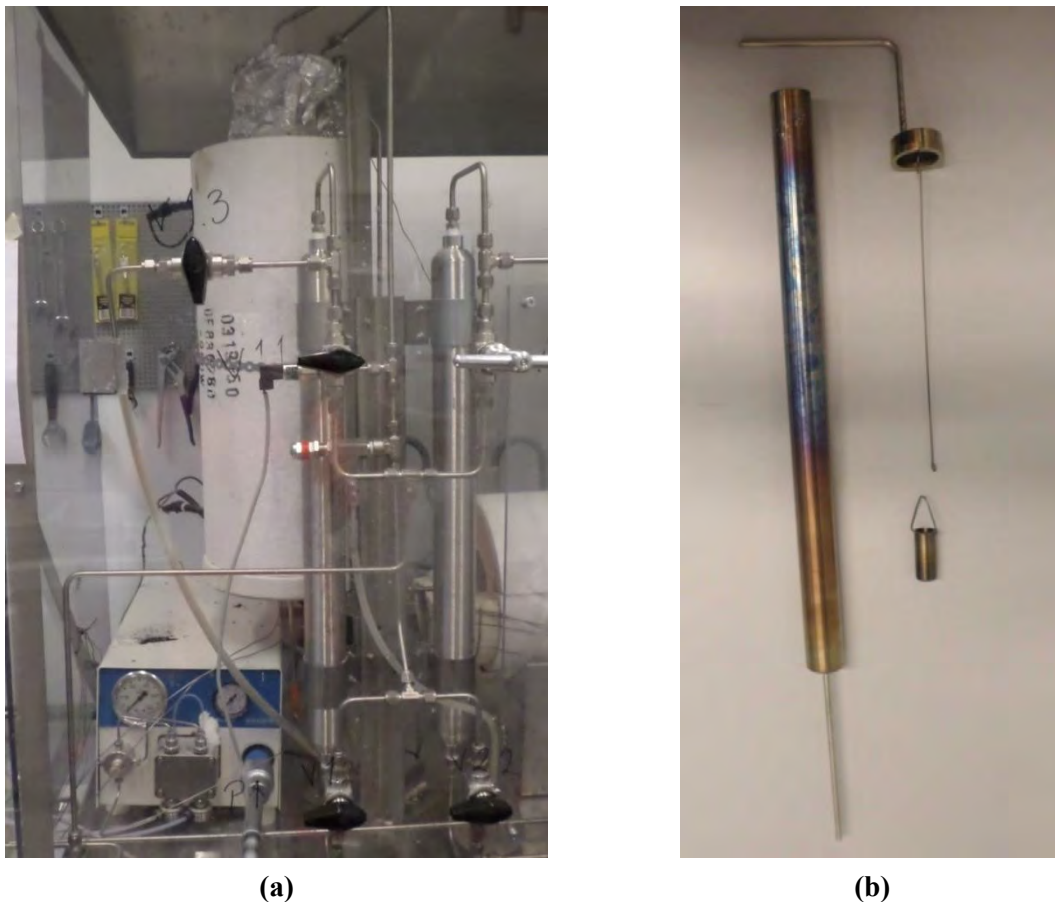


Figure 4.5. Photograph of the pyrolysis reactor (a) assembled (b) disassembled.

comes out from the top. The column is equipped with a temperature control, and everything is closed with a lid. This scheme is pretty similar to the experimental setting described by Demirbas and Arin (2002).

In these experiments, there isn't any distinction between the four peat samples (it is possible to see in the previous analysis in § 4.1 that they are chemically and physically very similar). Before each pyrolysis, the sample is ground, dried and mixed as described in § 4.1.4.

A slow pyrolysis (or conventional pyrolysis) is performed: this means that the heating rates are slow, the vapour residence time is long, and it is expected to have high yield of solid materials and very low yield of tar.

Pyrolysis is conducted at four different temperatures in the range of 150°C to 500°C in atmospheric pressure. The effect of different residence times is also studied: in the first round, the pyrolysis is conducted with a theoretical residence time equal to 0 minute (so the sample is kept in the reactor until the temperature reaches the desired value, and removed “immediately”); in the second round, the

residence time is equal to 10 minutes (hypothetically sufficient for the possible secondary reactions to occur).

The heating rate is kept at its maximum value (9 990°C/hr) and the nitrogen flow is maintained constant for all the experiments.

The resulting char is then weighed and analysed; its heat of combustion, ash and carbon contents are measured (Figure 4.6).



Figure 4.6. Photograph of the char after a pyrolysis at different temperatures and residence times.

The results of the experiments are reported in Table 4.10 (sample B used) and Table 4.11 (sample D used).

Each column corresponds to a pyrolysis at certain temperature and certain residence time. In these tables there are reported the mass of the container of the peat (m_{tank}), the mass of peat before the pyrolysis (m_{peat}) and the mass of the peat after the pyrolysis (m_{char}). The first temperature ($T_{settled}$) is the one defined for the experiment, while $T_{max, reached}$ is the maximum temperature reached during the pyrolysis with a residence time of 10 minutes (an overshoot is registered during the temperature control).

Table 4.10. Results of the pyrolysis of the sample B at different temperatures and residence times.

	residence time		residence time		residence time		residence time	
	0 min	10 min	0 min	10 min	0 min	10 min	0 min	10 min
m tank (g)	42.6468	42.6458	42.6459	42.6472	42.6466	42.646	42.647	42.6473
m peat (g)	1.6836	1.7817	1.8266	1.8142	1.7008	1.8783	1.8159	1.9096
T settled (°C)	150	150	267	267	383	383	500	500
T max reached (°C)	150	224	267	346	383	447	500	529
m char (g)	1.6809	1.762	1.8176	1.4868	1.6556	1.2523	1.4625	0.9445
m organic, A (g)	1.60	1.70	1.74	1.73	1.62	1.79	1.73	1.82
m organic, B (g)	1.60	1.68	1.73	1.40	1.58	1.16	1.38	0.85
y₁ (%)	99.83	98.84	99.48	81.06	97.21	65.03	79.58	46.97

Table 4.11. Results of the pyrolysis of the sample D at different temperatures and residence times.

	residence time		residence time		residence time		residence time	
	0 min	10 min	0 min	10 min	0 min	10 min	0 min	10 min
m tank (g)	42.65	42.65	42.67	42.65	42.65	42.65	42.65	42.65
m peat (g)	1.67	1.51	1.55	1.67	1.72	1.78	1.74	1.47
T settled (°C)	150	150	267	267	383	383	500	500
T max reached (°C)	150	229	267	343	383	444	500	539
m char (g)	1.66	1.49	1.54	1.52	1.68	1.27	1.62	0.68
m organic, A (g)	1.59	1.44	1.48	1.59	1.64	1.70	1.66	1.40
m organic, B (g)	1.58	1.42	1.47	1.44	1.60	1.19	1.54	0.61
y₁ (%)	99.37	98.61	99.32	90.58	97.56	69.94	92.76	43.61

Assuming that the char contains the same amount of ash of the original peat (in percentage, $A_d=4.70\%$ from Table 4.9), the organic masses are calculated in the following way:

$$m_{organic,A} = m_{peat} - (m_{peat} \cdot A_d) \quad [g] \quad (4.9)$$

$$m_{organic,B} = m_{char} - (m_{peat} \cdot A_d) \quad [g] \quad (4.10)$$

Where $m_{organic,A}$ is referred to the peat before the pyrolysis, while $m_{organic,B}$ to the char after the pyrolysis.

The organic yield y_1 indicates the amount of char that can be obtained from the peat at certain temperature and residence time; it is calculated with the formula:

$$y_1 = \frac{m_{organic,B}}{m_{organic,A}} \cdot 100 \quad [\%] \quad (4.11)$$

The resulting values at different residence times are reported in Figure 4.7 (for sample B) and Figure 4.8 (for sample D) as a function of the pyrolysis temperature.

As can be seen, the amount of char left decreases with an increase of the pyrolysis temperature in the range of 150 to 500°C, but this decreasing with a residence time of 10 minutes is faster than the one with a residence time of 0 minutes. This means that a longer residence time permits the occurrence of reactions like, for example, the release of volatiles. However, at 150 °C no reaction occurs even by increasing the residence time: the temperature is too low for the formation of char. Instead, if the temperature is higher, the difference between the yield at the two residence times increases.

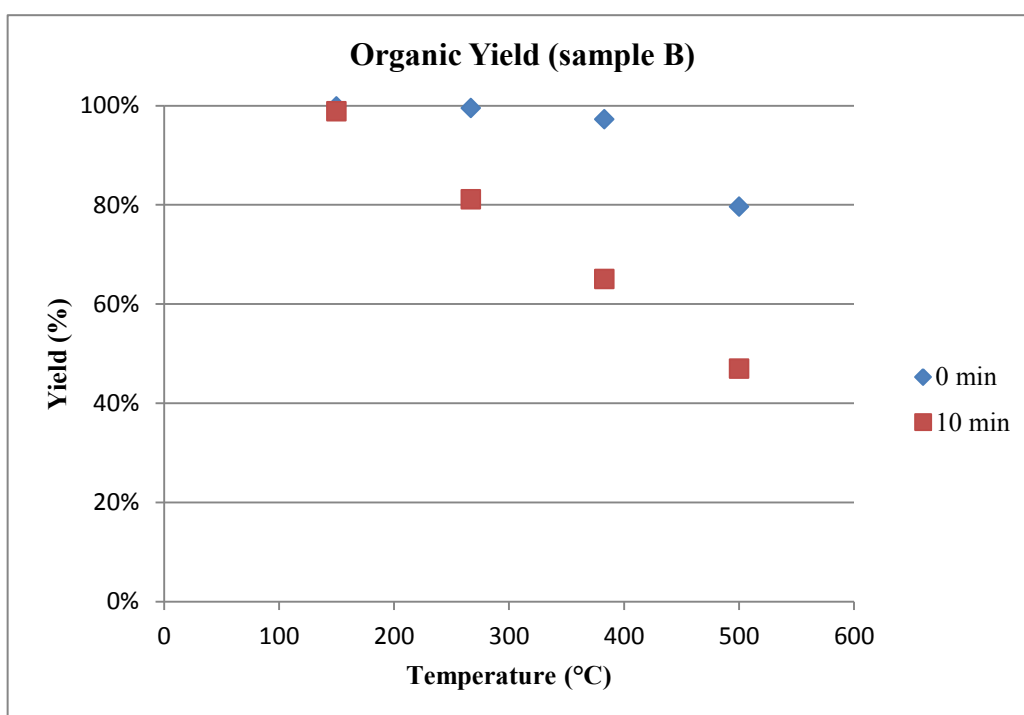


Figure 4.7. Organic yield of the pyrolysis of peat at different residence times as a function of the final temperature (sample B).

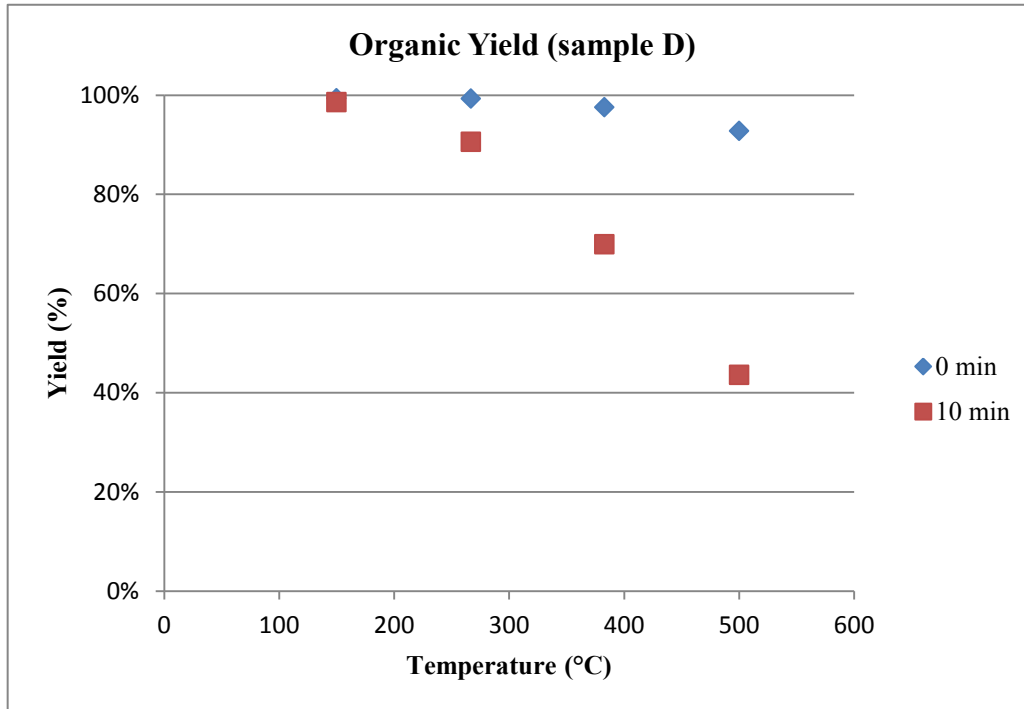


Figure 4.8. Organic yield of the pyrolysis of peat at different residence times as a function of the final temperature (sample D).

The calorific value of the char is measured with an oxygen bomb calorimeter (method described in § 4.1.2). The measurement is done with an amount of peat equal to m_1 , which corresponds to almost half of the whole pyrolyzed peat left (m_{char}), so it can be considered a good description of the char.

From the values of $\Delta H_{c,char}$, it is possible to see that, for sample B, at every temperature and every residence times (excluded $T=267$ °C, 0 min), the hypothetic heat that will be released in the complete combustion of the char is larger than the one released with the peat.

The energy yield y_2 is calculated with the following formula:

$$y_2 = \frac{m_{char} \cdot \Delta H_{c,char}}{m_{peat} \cdot \Delta H_{c,dry}} \cdot 100 \quad [\%] \quad (4.12)$$

where $\Delta H_{c,char}$ is the heat of combustion of the char measured with the oxygen bomb calorimeter (in MJ/kg_{dry}, from Table 4.12 and

Table 4.13), while $\Delta H_{c,dry}$ is the heat of combustion of the peat (equal to 22.55 MJ/kg_{dry}, from Table 4.9).

Table 4.12. Measurements of the heat of combustion of char obtained from the peat pyrolysis (conducted at different temperatures and residence times) (sample B).

	residence time		residence time		residence time		residence time	
	0 min	10 min	0 min	10 min	0 min	10 min	0 min	10 min
T settled (°C)	150	150	267	267	383	383	500	500
m peat (g)	1.6836	1.7817	1.8266	1.8142	1.7008	1.8783	1.8159	1.9096
m char (g)	1.6809	1.762	1.8176	1.4868	1.6556	1.2523	1.4625	0.9445
m sample (g)	0.7738	0.7624	0.7398	0.7539	0.6555	0.7296	0.7646	0.7218
ΔH (MJ/kg_{dry})	22.9092	22.998	21.1683	25.0061	23.3252	27.7466	27.5771	28.6967
y₂ (%)	106.6	106.0	98.2	95.5	105.8	86.2	103.5	66.2

Table 4.13. Measurements of the heat of combustion of char obtained from the peat pyrolysis (conducted at different temperatures and residence times) (sample D).

	residence time		residence time		residence time		residence time	
	0 min	10 min	0 min	10 min	0 min	10 min	0 min	10 min
T settled (°C)	150	150	267	267	383	383	500	500
m peat (g)	1.67	1.51	1.55	1.67	1.72	1.78	1.74	1.47
m char (g)	1.66	1.49	1.54	1.52	1.68	1.27	1.62	0.68
m sample (g)	0.6203	0.6233	0.5979	0.655	0.6249	0.6031	0.613	0.5561
ΔH (MJ/kg_{dry})	20.983	21.288	20.3958	22.1229	20.8895	25.1179	22.2304	26.3348
y₂ (%)	97.2	97.9	94.4	93.8	95.1	83.5	96.5	56.8

The resulting yields are reported in Figure 4.9 and Figure 4.10 as a function of the pyrolysis temperature and residence time.

It can be noticed that the energy yield decreases in all cases (excluded for sample B with a residence time of 0 min). This means that the theoretical heat of combustion that it is possible to obtain from the char is lower than the one obtained with the peat; the heat of combustion should decrease as little as possible and therefore a pyrolysis with a short residence time is preferred.

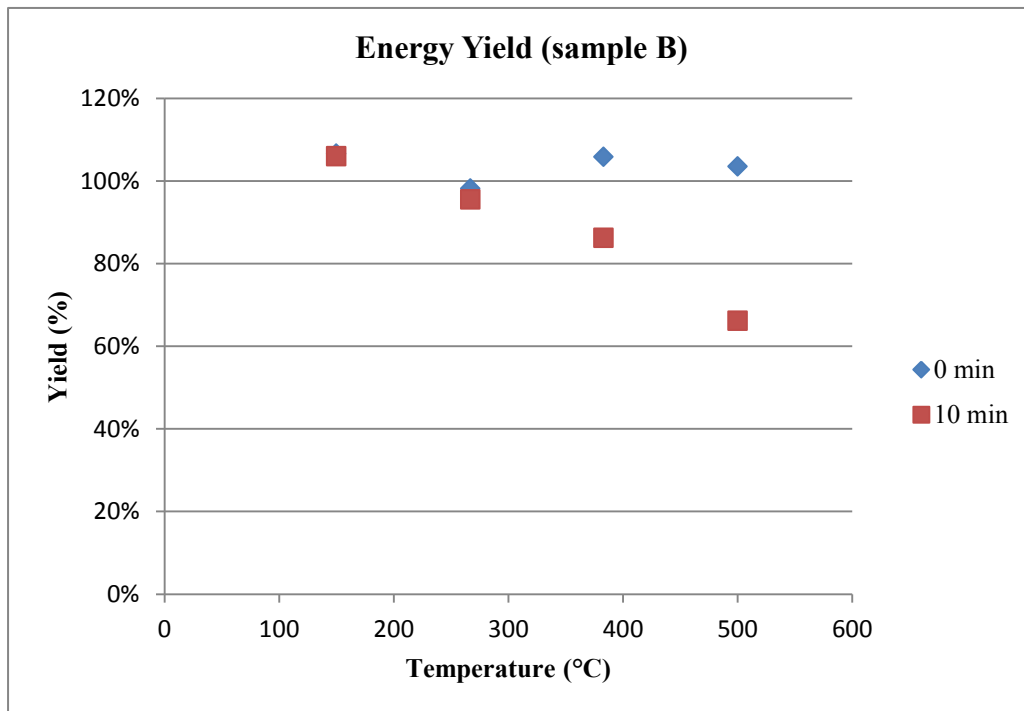


Figure 4.9. Energy yield of the pyrolysis of peat at different residence times as a function of the temperature (sample B).

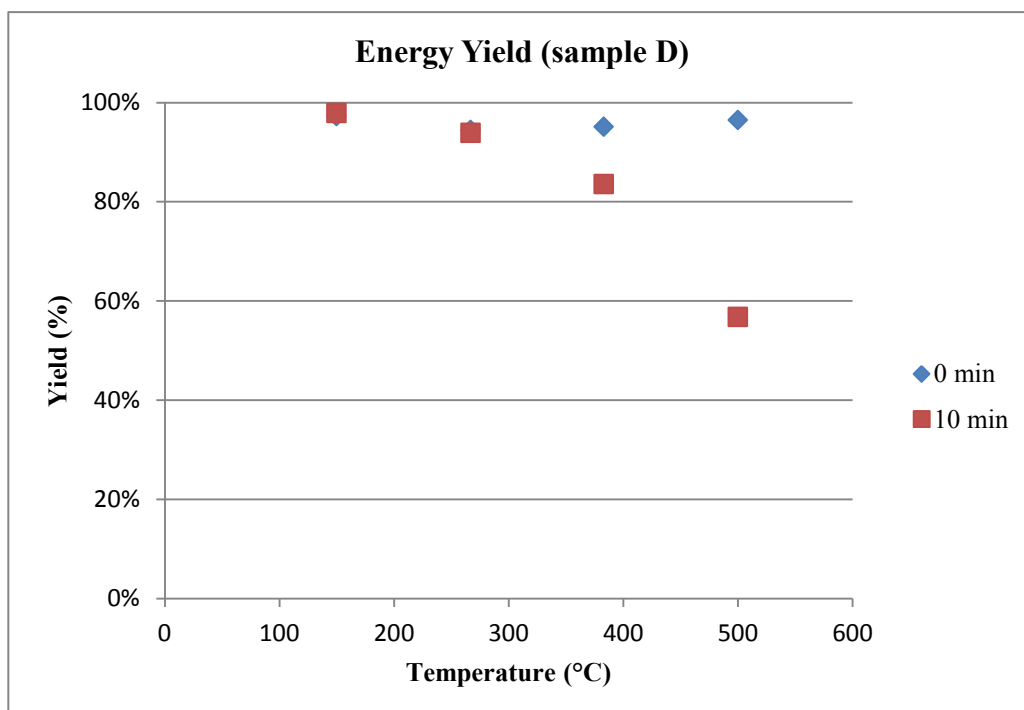


Figure 4.10. Energy yield of the pyrolysis of peat at different residence times as a function of the temperature (sample D).

However, it has to be taken in account that this yield is influenced by the resulting mass of char after the pyrolysis. With a longer residence time, the amount of char

is lower and the yield is influenced by this (even if, for example, the value divided by the mass is larger).

The elemental composition of the char was measured with the Elemental Analyser (procedure described in § 4.1.4). The resulting mass percentage of the carbon is reported in Table 4.14 (sample B) and Table 4.15 (sample D).

Table 4.14. Measurements of the carbon content of the char obtained from the peat pyrolysis (conducted at different temperatures and residence times) (sample B).

	residence time		residence time		residence time		residence time	
	0 min	10 min	0 min	10 min	0 min	10 min	0 min	10 min
T settled (°C)	150	150	267	267	383	383	500	500
m peat (g)	1.6836	1.7817	1.8266	1.8142	1.7008	1.8783	1.8159	1.9096
m char (g)	1.6809	1.762	1.8176	1.4868	1.6556	1.2523	1.4625	0.9445
% Carbon (weight)	44.66	51.14	58.21	53.51	52.68	52.65	83.43	73.88
y₃ (%)	84.51	95.86	109.80	83.12	97.20	66.54	127.37	69.26

Table 4.15. Measurements of the carbon content of the char obtained from the peat pyrolysis (conducted at different temperatures and residence times) (sample D).

	residence time		residence time		residence time		residence time	
	0 min	10 min	0 min	10 min	0 min	10 min	0 min	10 min
T settled (°C)	150	150	267	267	383	383	500	500
m peat (g)	1.67	1.51	1.55	1.67	1.72	1.78	1.74	1.47
m char (g)	1.66	1.49	1.54	1.52	1.68	1.27	1.62	0.68
% Carbon (weight)	50.29	53.49	48.06	46.74	43.09	56.76	51.52	56.93
y₃ (%)	94.75	100.04	90.52	80.64	79.77	76.76	90.93	49.92

The carbon yield y_3 is then calculated in the following way:

$$y_3 = \frac{m_{char} \cdot w_{C,char}}{m_{peat} \cdot w_{C,peat}} \cdot 100 \quad [\%] \quad (4.13)$$

where $w_{C,char}$ is the mass percentage of carbon in the char (from Table 4.14 and Table 4.15), and $w_{C,peat}$ is the mass percentage of the carbon in the peat (52.75%, from Table 4.9).

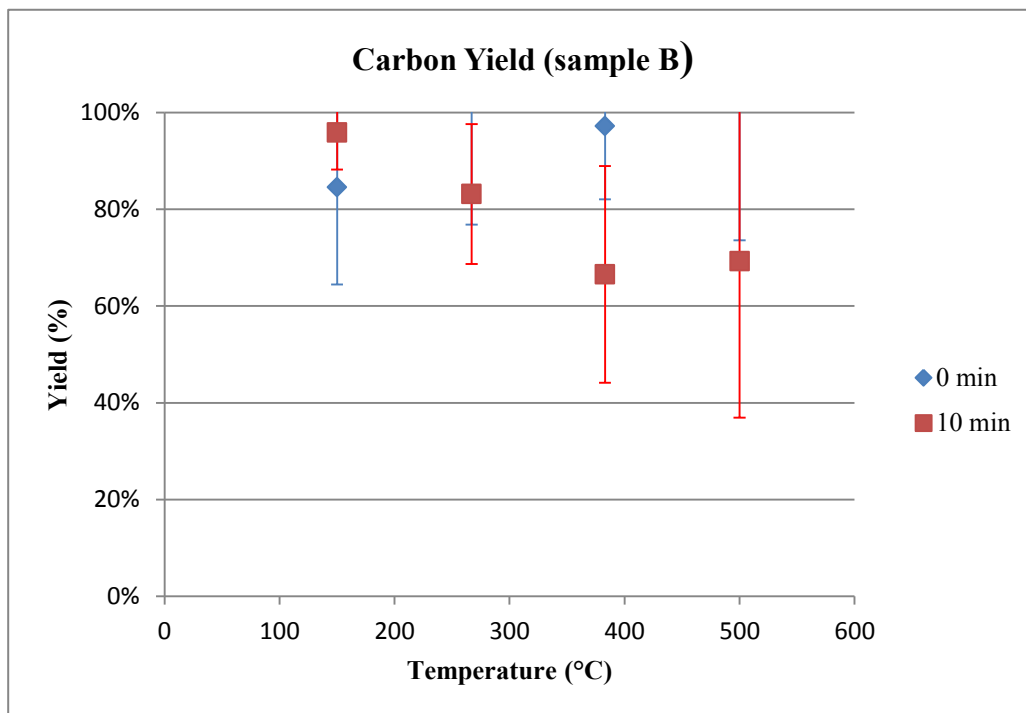


Figure 4.11. Carbon yield of the pyrolysis of peat at different residence times as a function of the temperature (sample B).

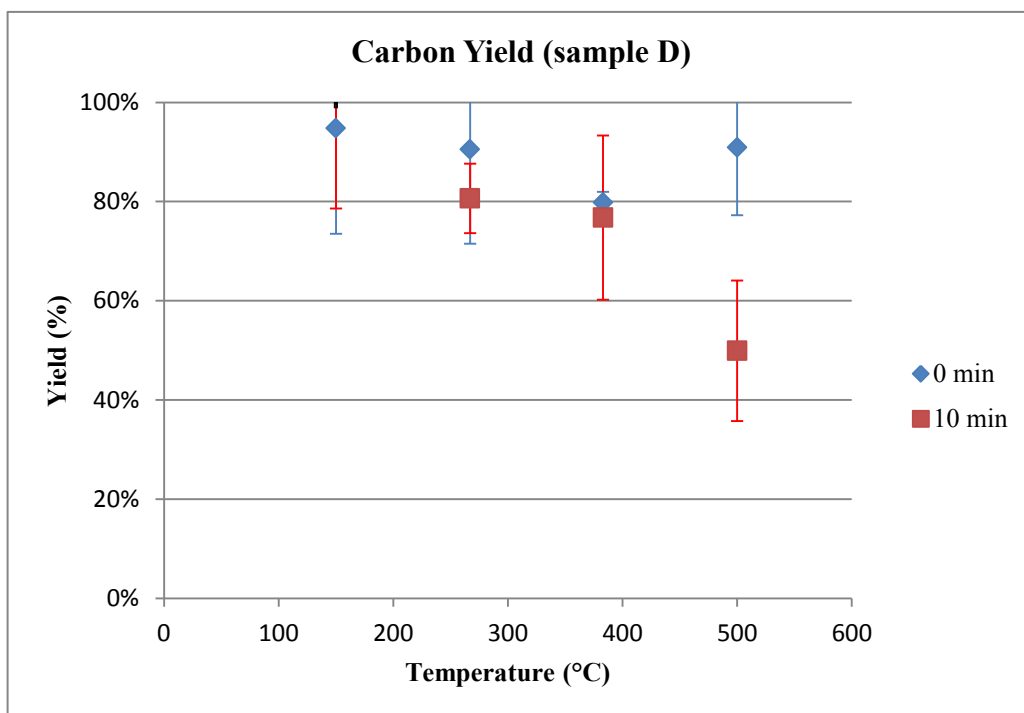


Figure 4.12. Carbon yield of the pyrolysis of peat at different residence times as a function of the temperature (sample D).

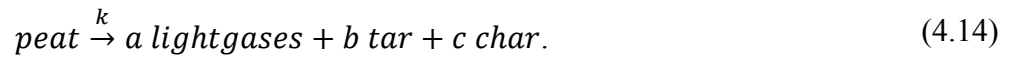
The resulting yields are reported in Figure 4.11 and Figure 4.12 as a function of the pyrolysis temperature and residence time. In these graphs the error in the measurement of the carbon content in the char is reported: during the experience

in the laboratory, indeed, it has been noticed that the CHNS Analyzer started to have some problems in its functionality at the end of the work, giving very different values for the percentages of the elements in the char. The method to calculate these errors is reported in § Appendix A. Notice that the measurements are always affected by experimental errors, so a yield that is bigger than 1 is a value without a real meaning.

The composition of the char depends on the type of the peat used and on the final temperature to which it is heated. In both cases (using sample B or sample D), the carbon yield decreases with higher temperature if the residence time is equal to 10 minutes; nevertheless, the results of the pyrolysis with a null residence time is very different. With the sample B, the tendency of the measurements seems that increases with the temperature, while it decreases by increasing the temperature with the sample D.

4.3 Mass balances

During the experiments, no tar was found in the char or in the reactor; and the composition of the gases was not measured; due of these, in order to further simplify, the secondary reaction is neglected and it is considered that peat decomposes just in char and gases (ash-free material), with the same kinetic constant. The single step first order reaction model is used then.



As it was said before, no tar was found in the products, so $b = 0$.

The mass balance of decomposition of the peat is:

$$\frac{dm_{peat}}{dt} = -k \cdot m_{peat} \quad (4.15)$$

In the other side, the mass balance of the char is:

$$\frac{dm_{char}}{dt} = c \cdot k \cdot m_{peat} \quad (4.16)$$

while the mass balance of the gases is:

$$\frac{dm_{gases}}{dt} = a \cdot k \cdot m_{peat} \quad (4.17)$$

To determine the kinetic constant k , the mass balance of peat is used. With a simple integration, it is possible to linearize the equation:

$$\ln(m_{peat})_t = \ln(m_{peat})_0 - k \cdot t. \quad (4.18)$$

For each temperature, two measurements are available: one at residence time equal to 0, the other one at 10 minutes; a straight line can be drawn from this data and the kinetic constant is its slope.

$$k = -\frac{(\ln(m_{peat})_t - \ln(m_{peat})_0)_{t=10} - (\ln(m_{peat})_t - \ln(m_{peat})_0)_{t=0}}{10} \quad (4.19)$$

The results for both samples are reported in Table 4.16.

Table 4.16. *Calculated kinetic constants at different temperatures for samples B (a) and D (b).*

T (°C)	k (1/min)
150	0.0010
267	0.0204
383	0.0402
500	0.0527

(a)

T (°C)	k (1/min)
150	0.0008
267	0.0092
383	0.0332
500	0.0756

(b)

At this point, it is assumed that the kinetic constant follows the Arrhenius equation; then, the next formula is valid.

$$\ln(k) = -\frac{E_a}{R} \cdot \frac{1}{T} + \ln(A) \quad (4.20)$$

From Table 4.16, the graphs in Figure 4.14 and Figure 4.13 for the two samples can be drawn:

In the equation of the trend lines the slope m is equal to:

$$m = \frac{-E_a}{R} \rightarrow E_a = -m \cdot R \quad (4.21)$$

where R is the ideal gas constant ($R = 8.314 \text{ kJ/kmol K}$); instead, the intersection q with the y axis is:

$$q = \ln(A) \rightarrow A = e^q. \quad (4.22)$$

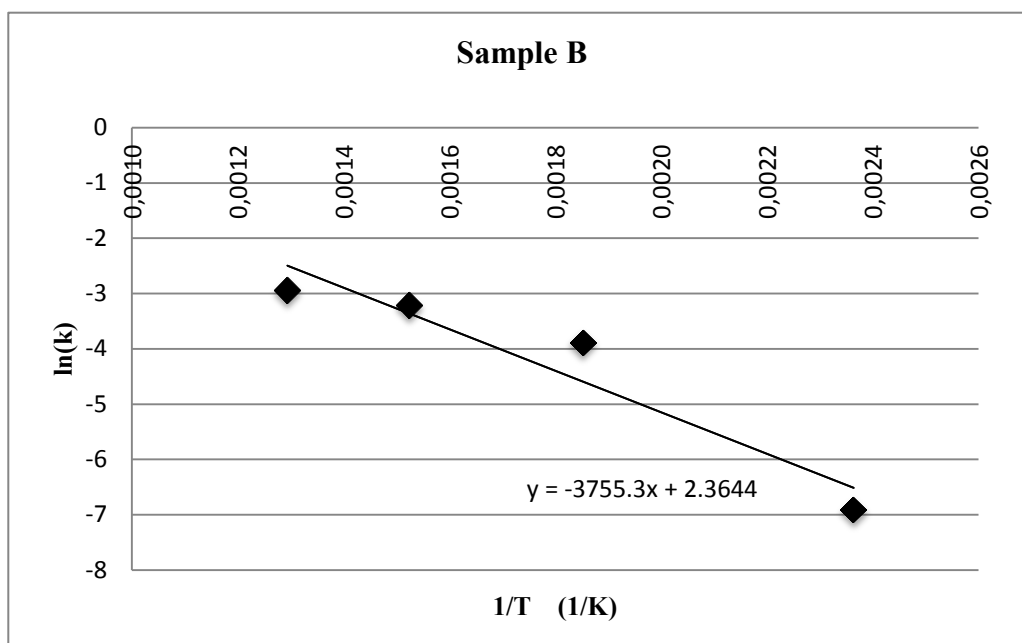


Figure 4.14. Dependence of $\ln(k)$ on the reciprocal of the temperature (sample B).

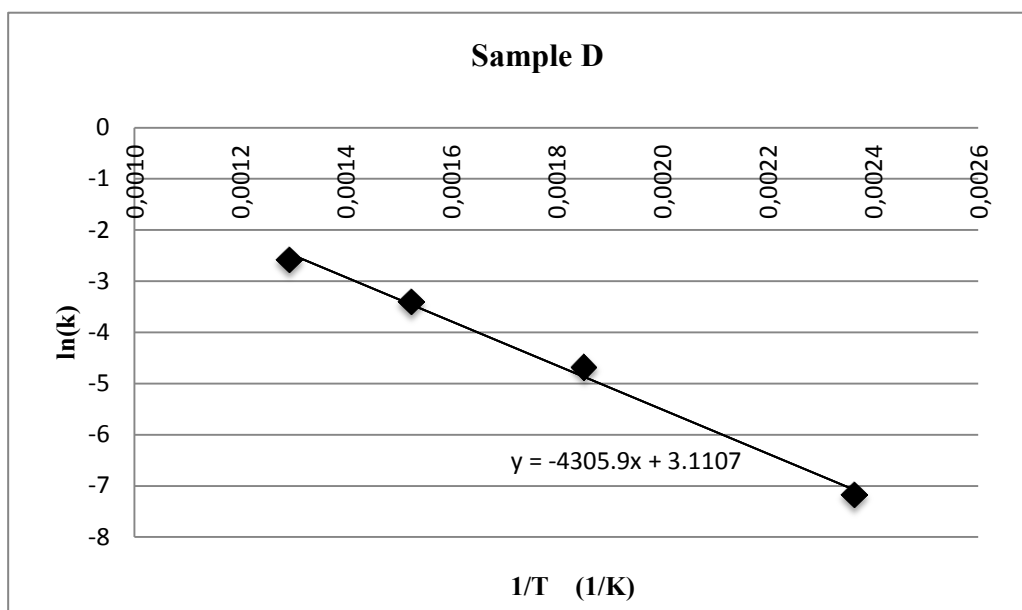


Figure 4.13. Dependence of $\ln(k)$ on the reciprocal of the temperature (sample D).

Results are reported in Table 4.17.

Table 4.17. Activation energy and pre-exponential factor of the kinetic constants for samples B and D.

SAMPLE	Ea (kJ/kmol)	A (1/min)
B	31222	10.6
D	35800	22.4

These values are quite reasonable: according to Roy et al. (1983), the activation energy for the peat pyrolysis is between 8 and 14 kcal/mol, that is nearly 33 490 and 58 620 kJ/kmol.

Then, the average kinetic constant for peat is:

$$k = 16.5 \cdot e^{\frac{-33511}{8.314 \cdot T}} \quad [1/\text{min}] \quad (4.23)$$

4.4 Energy balances

A precise energy balance cannot be calculated because some experimental data have not been measured. However, a simple estimation of the amount of energy used can be made by analysing the energy yield.

In the beginning of the pyrolysis, the system has an amount of energy equal to:

$$E_1 = m_{peat} \cdot \Delta H_{c,dry} \quad [\text{MJ}] \quad (4.24)$$

while in the end it is:

$$E_2 = m_{char} \cdot \Delta H_{c,char} \quad [\text{MJ}] \quad (4.25)$$

The theoretical energy needed to pyrolyse the peat (at a certain temperature and residence time) is described as.

$$\Delta E = E_1 - E_2 \quad [\text{MJ}] \quad (4.26)$$

The results are reported in Figure 4.15 and Figure 4.16.

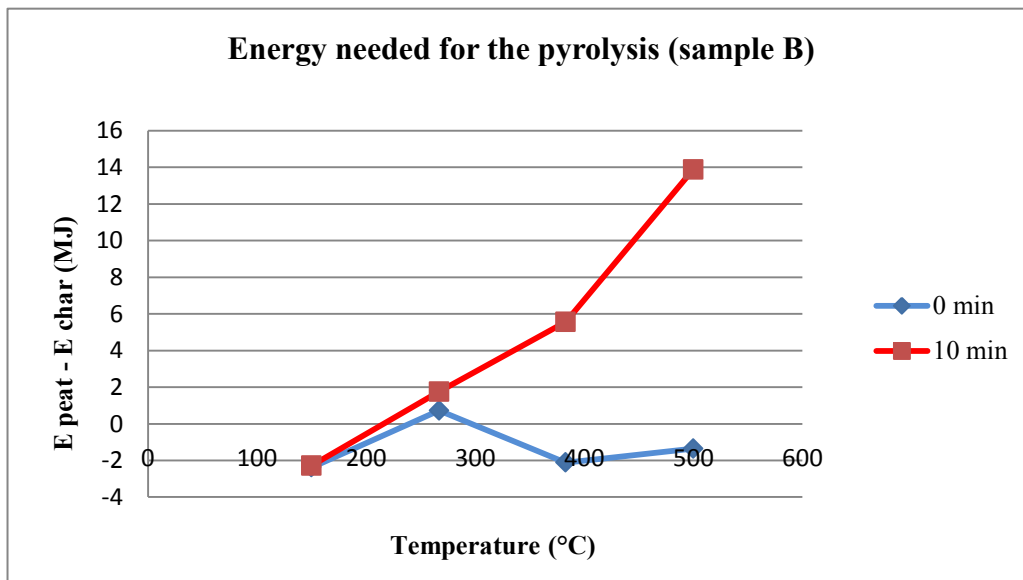


Figure 4.15. Energy needed for the pyrolysis of sample B, for each final temperature and residence time.

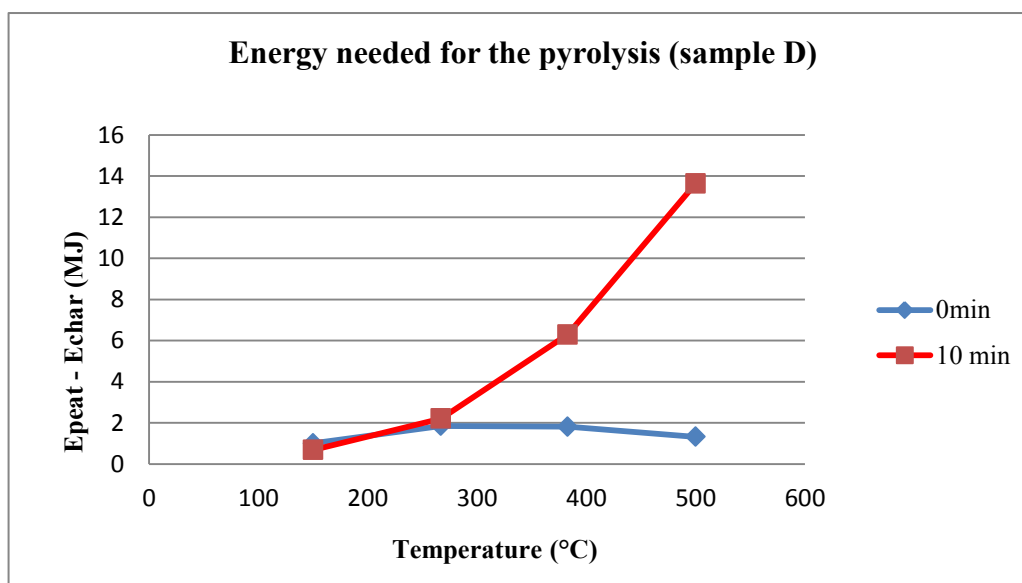


Figure 4.16. Energy needed for the pyrolysis of sample D, for each final temperature and residence time.

The amount of energy needed for the pyrolysis increased a lot with the temperature when the residence time is equal to 10 minutes. In the previous experiments, it has been pointed out that char at higher temperature and higher residence time has better characteristics than the one at lower residence time (as a major carbon content or a higher heat of combustion), but its production requires a very big energy amount, also because the char produced is smaller. That makes the pyrolysis process not so convenient in an industrial scale: it is necessary to use a lot of energy in order to have high quality carbon, but in small amounts. This consideration defines the conditions of pyrolysis: char from high temperature/residence time pyrolysis is too much costly to be used as a fuel, so it will be preferably use in markets where the final application requires a certain quality (catalysis, electrochemical process, adsorption...).

Conclusions

Peat pyrolysis is a complex process where it is hard to predict theoretically the amount and the types of substances produced without having experimental data. In this experimental work the influence of some parameters on the yield of char produced is shown, in particular the role of temperature and residence time in the reactor is investigated. The interest was to see the variation on the characteristics of the char produced (above all, its heat of combustion and the carbon content), in order to find the best conditions to have char suitable for other process.

Char with the highest carbon content is produced at 500°C and short residence time, while char with the highest heat of combustion is produced at 500°C and long residence time, but at this temperature the organic yield decreases deeply. That means that, starting from a certain amount of peat, the mass of char produced is smaller than at a lower temperature; therefore, the energy required increases almost exponentially while the temperature goes above 400°C. Depending on the destination of char, the pyrolysis conditions have to be settled: coke used in domestic heating is produced by pyrolysis at low temperatures, because it is not economically convenient to use such amount of energy for this final use. Char with a very high percentage of carbon, instead, can be used to form anodes in electrochemical cells, or as a catalyst support: in these cases, the final destination can justify the high production costs.

There are, however, some other practical considerations to make if a substitution of peat with char as a raw material for chemical process is desired. First, the char is not hygroscopic as peat, so the storage and the transport of it is easier (the moisture content of the material largely affects the thermal efficiency of the process). Second, the heat of combustion of char is bigger than the one of peat: a comparison of them in dry-basis was previously made in § 4.1.2. Other things to consider are the removal of water from peat (but it counts in the pre-treatment of the feedstock for the pyrolysis too) and the ash content of peat and char (that has to be below 6% to avoid slagging and obstructions in the reactor).

Referring to this specific work, the main difficulties were found in the pyrolysis experiment: the equipment was new and a prototype. It was not possible to

measure the flow of gases that goes out from the reactor (neither its composition): these data would be useful for better energy and mass balances. The difficulties with the CHNS Analyzer during the analysis of the composition of peat were described already in § 4.2 ; in addition, it has to be taken in account that peat is an extremely heterogeneous material, and it is hard to have a meaningful sample. This problem has to be considered in industrial applications: it is impossible to have a standard production (with a feedstock that has always the same characteristics), because the properties and the composition of the raw material vary a lot with the decomposition degree, the history and the geographical origin of the peat, etc., and this causes great variation in the yields and in the final quality of the char.

For a future work, it would be interesting to measure the flow and the composition of the gases in order to calculate precise energy and mass balances and to build a pyrolysis model. In addition, the char produced can be utilised in some laboratory experiments (as gasification) to see which products can be obtained and the problematics of this raw material in this kind of process. With a more suitable equipment, higher temperatures can be reached and some tar can be obtained and studied, too. Therefore, in this study only “moderately decomposed peat” has been used: in the future experiments, peat with different decomposition degree as pyrolysis feedstock can be used to observe its influence in yields and type of products.

In the end, due of these problematics and the high energy costs, the pyrolysis of peat in order to create char is not convenient, but can be interesting if it is accompanied to other process (with the recovery of tars and gases) that can cover the cost of coking. In this way, the coke can become an interesting carbon source for industries who wants to find a more sustainable feedstock.

Nomenclature

A	= Pre-exponential factor of the Arrhenius equation (1/min)
A_d	= Ash content (%)
A_i	= Area of the peak given by the chromatograph
E_1	= Energy of the system before pyrolysis (MJ)
E_2	= Energy of the system after pyrolysis (MJ)
E_a	= Activation energy of the Arrhenius equation (kJ/kmol)
f_i	= Correcting factor for the i th element (g)
k	= Kinetic constant of the Arrhenius equation (1/min)
m	= Slope of the line
m_0	= Mass of wet peat (g)
m_1	= Mass of dry peat (g)
m_2	= Mass of ashes of peat (g)
m_{char}	= Mass of char (produced by pyrolysis) at a certain time (g)
m_{gases}	= Mass of gases (produced by pyrolysis) at a certain time (g)
m_i	= Mass of the i th element (g)
$m_{organic,A}$	= Mass of peat in ash-free material basis (g)
$m_{organic,B}$	= Mass of char in ash-free material basis (g)
m_{peat}	= Mass of peat at a certain time (g)
m_{solids}	= Mass of biomass at a certain time (g)
m_{std}	= Mass of Sulphanilamide (g)
m_{tar}	= Mass of tar (produced by pyrolysis) at a certain time (g)
MC	= Moisture content (%)
MW_i	= Molar weight of the i th element (kg/kmol)
q	= Intersection of the line with the y-axis
R	= Gas constant (8.314 kJ/kmol K)
t	= Time (min)
T	= Temperature (°C)
$w_{C,char}$	= Mass fraction of carbon in char
$w_{C,peat}$	= Mass fraction of carbon in peat
w_i	= Mass fraction of the i th element
x_i	= Molar percentage of the i th element (%)
y_1	= Organic yield (%)

- y_2 = Energy yield (%)
- y_3 = Carbon yield (%)
- ΔE = Energy used for pyrolysis (MJ)
- $\Delta H_{c,bio}$ = Heat of combustion of peat on ash-free material basis (MH/kg_{bio})
- $\Delta H_{c,char}$ = Heat of combustion of char on dry basis (MH/kg_{bio})
- $\Delta H_{c,dry}$ = Heat of combustion of peat on dry basis (MH/kg_{dry})
- $\Delta H_{c,measured}$ = Heat of combustion of peat on wet basis (MH/kg)

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Appendix A

In this section the calculations of the errors of the graphs in § Chapter 4 are explained.

As said before, the CHNS Analyzer in the end of the experiments started to be not accurate as in the beginning: it is supposable that the values of the carbon content in the char are not precise, so the error in these measurements has to be calculated.

For each sample of char (at a certain temperature and residence time), three measurements of the carbon content are made. The percentages reported in Table 4.14 and in Table 4.15 are the averaged value of these three measures, while the standard deviation of the sample are calculated with the formula:

$$\sigma_w = \sqrt{\frac{\sum (w_{C,char} - \bar{w}_{C,char})^2}{(n - 1)}} \quad (\text{A.1})$$

where $w_{C,char}$ is the percentage of carbon in the char of a single measure, $\bar{w}_{C,char}$ is the averaged value of the three measures and n is the number of the measurements made (so $n = 3$). The standard deviations at each temperature and residence time are reported in Table A.1.

Table A.1. Standard deviations of the measurements of the carbon content in the char (both samples B and D).

	residence time		residence time		residence time		residence time	
	0 min	10 min	0 min	10 min	0 min	10 min	0 min	10 min
T settled (°C)	150	150	267	267	383	383	500	500
σ_w (sample B)	10.60%	4.08%	17.46%	9.31%	8.22%	17.71%	35.23%	34.49%
σ_w (sample D)	11.29%	11.45%	10.09%	4.06%	1.18%	12.25%	7.76%	16.17%

The errors in percentage are then calculated by using the formula (4.13) of the carbon yield seen in § 4.2 :

$$e_{y_3} = \left(\frac{m_{char} \cdot (\bar{w}_{C,char} + \sigma_w)}{m_{peat} \cdot w_{C,peat}} \cdot 100 \right) - \left(\frac{m_{char} \cdot \bar{w}_{C,char}}{m_{peat} \cdot w_{C,peat}} \cdot 100 \right) \quad (\text{A.2})$$

The results (reported in Table A.2) are the values for the errors in Figure 4.11 and Figure 4.12.

Table A.2. *Errors of the carbon yield caused by a malfunctioning of CHNS Analyzer (both samples B and D).*

	residence time		residence time		residence time		residence time	
	<i>0 min</i>	<i>10 min</i>	<i>0 min</i>	<i>10 min</i>	<i>0 min</i>	<i>10 min</i>	<i>0 min</i>	<i>10 min</i>
T settled (°C)	150	150	267	267	383	383	500	500
e_{y3} (sample B)	20.06%	7.64%	32.94%	14.46%	15.16%	22.39%	53.79%	32.34%
e_{y3} (sample D)	21.28%	21.42%	19.00%	7.00%	2.19%	16.57%	13.70%	14.18%